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CORRELATION OF VAPOR PHASE THERMODYNAMIC PROPERTIES

BY

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled CORRELATION OF VAPOR PHASE THERMODYNAMIC PROPERTIES by Ronald T. Clare, B.Sc. in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

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ABSTRACT

This thesis presents an investigation of a variety of
equation of state forms for pure components. The investiga-
tion was undertaken in order to develop an equation of state
which would adequately describe, not only the P-V-T behavior
over wide ranges of pressure and temperature, but also derived
properties such as enthalpy departure and fugacity.

The best equation of state form was found to be a
fifteen constant expansion, based upon a modified form of the
Martin-Hou equation. The equation of state was fitted, over
wide ranges of pressure and temperature, for eight gases, with
good results. The equation of state was restricted to the
vapor phase because of a drastic loss of accuracy encountered
when trying to represent two phases with one set of equation
constants.

A method of obtaining improved thermodynamic property
representation is presented. The method showed merit, but
was hampered by a lack of adequate experimental thermodynamic
properties. The usefulness of the method, however, is apparent.

All data fitting required in this study was accomp-
lished using the Chebyshev criterion of best fit. Examples
of the data fitting procedure are presented in the form of
computer programs. Explanation of the use of the computer
programs is given.

ACKNOWLEDGEMENTS

INTRODUCTION

The motivation for this investigation of equations of state was supplied by the development of an alternate concept in data fitting. This fitting technique is described by P.K. Leung(13) and frames data fitting as a linear programming problem. The criterion of best fit used in this procedure is minimization of the maximum absolute or absolute percentage deviation. This is generally known as the Chebyshev criterion. Linear programming data fitting has several features which make it especially suitable for investigating equations of state.

The purpose of this investigation was to develop some general framework for an equation of state applicable to pure components. To be completely general, the equation form had to be applicable to all types of gases and able to cover as wide a range of pressures and temperatures as are normally encountered industrially.

An equation of state must satisfy two conditions in order to be applicable to a particular component. These conditions are:

1. It must provide an accurate representation of the volumetric behavior over the range of pressure and temperature to be fitted.

2. It should provide a reasonably accurate representation of the thermodynamic properties which can be derived from the volumetric behavior.

The first condition can usually be met with standard "least squares" fitting techniques, although the accuracy of the fit depends upon the range of variables required and the complexity of the approximating function used. Meeting the second condition is not so easy. Accurate representation of the volumetric properties does not guarantee equally accurate representation of all of the derived thermodynamic properties.

An analysis of the relative accuracy of calculated thermodynamic quantities was made in order to obtain some insight into what kind of accuracy to expect for the various properties. A method for improving the accuracy of calculated thermodynamic properties was developed utilizing the linear programming data fitting procedure. This procedure, however, requires accurate experimentally determined thermodynamic properties which are consistent with a set of P-V-T data. Experimental data of this kind are generally hard to find.

LINEAR PROGRAMMING DATA FITTING

A detailed explanation of the linear programming data fitting procedure is given in the thesis by Leung(13). It is appropriate, however, to give a brief description of the concept, its solution and advantages, since linear programming data fitting was used almost exclusively in this thesis.

Consider the approximating function,

$$y_i = \alpha_j g_j(x_i)$$

where;

$g_j(x_i)$ are specified functions of x.

Using the Chebyshev criterion of best fit, the following problem can be formulated.

$$\left| f(x_i) - \sum_{j=1}^{n} \alpha_j g_j(x_i) \right| < \lambda \qquad 1 < i < m$$

where we wish to minimize λ maximum.

The absolute value restriction may be removed by the formation of positive and negative equations.

$$f(x_i) - \sum_{j=1}^{n} \alpha_j g_j(x_i) < \lambda \qquad 1 < i < m$$

$$- f(x_i) + \sum_{j=1}^{n} \alpha_j g_j(x_i) > -\lambda$$

Rearranging the two equations gives,

$$\lambda + \sum_{j=1}^{n} \alpha_j g_j(x_i) > f(x_i)$$

$$\lambda - \sum_{j=1}^{n} \alpha_j g_j(x_i) > - f(x_i)$$

The data fitting problem can now be formulated in the following linear programming form:

Minimize (λ) maximum, subject to;

1) $$\lambda + \sum_{j=1}^{n} \alpha_j g_j(x_i) > f(x_i) \qquad 1 < i < m$$

2) $$\lambda - \sum_{j=1}^{n} \alpha_j g_j(x_i) > - f(x_i)$$

With the introduction of slack and artificial variables the problem becomes;

minimize, $$Z = \lambda + M \sum_{i=1}^{m} u_i$$

where M is a penalty coefficient, subject to;

$$\lambda + \sum_{j=1}^{n} (y_{1_j} - y_{2_j}) g_j(x_i) - v_{1_i} + u_i = f(x_i)$$

$$\lambda - \sum_{j=1}^{n} (y_{1_j} - y_{2_j}) g_j(x_i) + v_{2_i} = -f(x_i)$$

$$1 < i < m$$

where V_{1_i}, V_{2_i} are the slack variables and u_i are the arti-
ficial variables. The variables α_j are not restricted in
sign so the substitution

$$\alpha_j = Y_{1_j} - Y_{2_j}$$

was made. Thus, all the variables λ, Y_{1_j}, Y_{2_j}, V_{1_i}, V_{2_i} and
u_i are non-negative.

The problem formulated can be solved directly by the
simplex method to obtain the optimum equation coefficients α_j.
However, if the number of data points m is very large, the
problem quickly becomes too large for practical computation.
A means of improving the computational efficiency of the prob-
lem is available through the application of dual linear pro-
gramming.

The rules for obtaining the dual of a linear programm-
ing problem may be summarized in the following table where;

     A - coefficient matrix for the constraint equations.

     b - constraint equation values for the primal problem.

     x - variables of the primal problem.

     C - objective function coefficients for the primal
          problem.

     Superscript T refers to the transpose of the matrix.

     y - variables of the dual problem.

Primal

	non-negative x_1 . . . . x_p	unrestricted x_{p+1} . . . . x_n		
1 . . . k	A	B	=	b_1 . . b_k
k+1 . . . k+r	C	D	$\leq$	b_{k+1} . . b_{k+r}
k+r+1 . . . k+r+s	E	F	$\geq$	b_{k+r+1} . . b_{k+r+s}
	c_1 . . . . c_p	c_{p+1} . . . . . . c_n		min. Z

Dual

	unrestricted y_1 . . . . . . y_k	non-negative y_{k+1} . . y_{k+1}	non-negative y_{k+r+1} . . . y_{k+r+s}		
1 . . . p	A^T	$-C^T$	E^T	$\leq$	c_1 . . . c_p
p+1 . . . p_n	B^T	$-D^T$	F^T	=	c_{p+1} . . . c_n
	b_1 . . . . . . b_k	$-b_{k+1}$ . . b_{k+r}	b_{k+r+1} . . . b_{k+r+s}		max. Z

Use of these tables requires that all b values in the primal be adjusted so that they are non-negative.

The duality theorem states that when the optimum solution to the dual problem has been found, the objective function value is equal to that of the optimum solution of the primal. The values of the dual problem variables bear no direct relationship to the primal variables. The primal variables, however, can be solved for by solving the set of constraint equations in the primal which correspond to non-zero dual variable values. The constraint equations become equalities when the dual variables corresponding to those equations are non-zero. The only non-zero variables in the linear program solution are the basic variables. Therefore, the constraint equations corresponding to the optimum solution basic variables can be made equality equations and solved for the optimum primal variable values.

The dual of the data fitting problem has the following form.

$$
\begin{array}{c}
\begin{array}{cccc} y_1 \cdots \cdots y_m & \quad y_{m+1} \cdots \cdots y_{2m} \end{array} \\
\begin{array}{c} 1 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ n \end{array}
\left[
\begin{array}{ccc|ccc}
1 \cdots \cdots 1 & 1 \cdots \cdots 1 \\
g_1(x_1) \cdots g_1(x_m) & -g_1(x_{m+1}) \cdots -g_1(x_{2m}) \\
\cdot & \cdot \\
\cdot & \cdot \\
\cdot & \cdot \\
g_n(x_1) \cdots g_n(x_m) & -g_n(x_{m+1}) \cdots -g_n(x_{2m})
\end{array}
\right]
\begin{array}{c} < \\ = \\ = \\ = \\ = \end{array}
\left[
\begin{array}{c} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{array}
\right] \\
\begin{array}{c} \left[f(x_1) \cdots f(x_m) \mid -f(x_{m+1}) \cdots -f(x_{2m}) \right] \quad = \quad Z \end{array}
\end{array}
$$

The objective function Z is to be maximized. All of the dual variables y_1 to y_{2m} are non-negative. To obtain a starting solution a slack variable is added to equation 1 and artificial variables are added to equations 2 to n. For the non-trivial case where $\lambda > 0$ the slack variable introduced in equation 1 must take a value of zero in the final solution. To insure this, equation 1 is made an equality equation and an artificial rather than a slack variable is added to the equation.

The optimum solution of the dual problem gives the optimum value of λ and the variables in the optimum basic solution tell at which data points the maximum λ value occurs. The constraint equations corresponding to the basic data points can then be made equality equations and solved for λ and the equation coefficients α_j. This requires the solution of a set of n+1 linear equations.

In the solution of a linear programming problem addition of variables costs very little in computation time while addition of constraints adds a great deal to computation time. For the data fitting problem the number of primal constraints is 2m, while for the dual the number of constraints is n+1, where m is the number of data points and n is the number of equation coefficients. Thus, solution of the dual of the data fitting problem represents a very significant gain in computational efficiency.

There are several characteristics of the linear pro-
gramming method of data fitting which are worthy of note:

1. The approximating function can be any linear combination
    of specified functions.

2. No specific data point spacing is required.

3. The data to be fitted must be well smoothed and error
    free for the results to be meaningful. However, large
    random errors can be detected by careful examination of
    the data points which control the fit. Several controlling
    data points occurring within a small range of the variables
    indicates a questionable data point. Data points in such
    a region should be graphically plotted in order to pin-
    point a possible error.

4. There are no computational difficulties encountered in
    solving for the equation coefficients, even for high
    order equations. The method does not suffer from the ill-
    conditioning problem encountered when fitting high order
    equations using "least squares".

5. Various constraints on the function fit such as deriva-
    tives of the function can readily be incorporated into
    the fitting procedure.

B-W-R EQUATION

The Benedict-Webb-Rubin equation of state has gained the widest acceptance; therefore, it was chosen as a convenient reference in evaluating the equations of state studied in this thesis. An extensive study of the B-W-R equation for propane was undertaken in order to establish the fitting accuracy of the equation. Various methods of fitting were used, including methods for improving enthalpy departure predictions.

The following results establish the accuracy of the pressure and enthalpy departure predictions of the B-W-R equation for propane. They also indicate the utility of the various fitting criteria.

Equations:

$$Z = 1.0 + (B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3})d + (b - \frac{a}{RT})d^2$$

$$+ \frac{a\alpha d^5}{RT} + \frac{cd^2}{RT^3}[(1 + \gamma d^2)e^{-\gamma d^2}]$$

$$(H - H_o)_T = J\{(B_o RT - 2A_o - \frac{4C_o}{T^2})d + (2bRT - 3a)\frac{d^2}{2}$$

$$+ \frac{6a\alpha d^5}{5} + \frac{cd^2}{T^2}[\frac{3 - 3e^{-\gamma d^2}}{\gamma d^2} - \frac{e^{-\gamma d^2}}{2}$$

$$+ \gamma d^2 e^{-\gamma d^2}]\}$$

J = conversion factor from units of PV to BTU/lb.

Data:

Propane - vapor region

P-V-T data(6)	P - 14.696 ⟶2057.44 psia
(237 points)	T - 545.67 ⟶1096.76 °R
$(H - H_o)_T$ data(21)	P - 200.00 ⟶1000.0 psia
(11 points)	T - 659.63 ⟶ 859.63 °R

Fitting Criteria

	1	2	3	4
A_o =	$.25980775 \times 10^5$	$.88471487 \times 10^4$	$.77471258 \times 10^4$	$.81509683 \times 10^4$
B_o =	$.14833089 \times 10^1$	$.12128731 \times 10^0$	$.18420332 \times 10^0$	$.17099770 \times 10^0$
C_o =	$.56938962 \times 10^{10}$	$.91613260 \times 10^{10}$	$.96361525 \times 10^{10}$	$.95383007 \times 10^{10}$
a =	$.40377788 \times 10^5$	$.11381319 \times 10^6$	$.78955402 \times 10^5$	$.68293160 \times 10^5$
b =	$.47479564 \times 10^1$	$.10426864 \times 10^2$	$.73152495 \times 10^1$	$.66016528 \times 10^1$
c =	$.20117470 \times 10^{11}$	$.34855595 \times 10^{11}$	$.28184636 \times 10^{11}$	$.26289272 \times 10^{11}$
$a\alpha$ =	$.11229799 \times 10^6$	$.16273998 \times 10^6$	$.13971655 \times 10^6$	$.13186063 \times 10^6$
γ =	$.5654 \times 10^1$	$.4510 \times 10^1$	$.4600 \times 10^1$	$.4800 \times 10^1$

	1	2	3	4
Max. % dev. in Z =	4.4413	3.8930	4.1442	3.4140
Max. abs. dev. in Z =	0.01876	0.01387	0.01409	0.0200
Ave. % dev. in Z =	0.7105	1.0755	0.9545	0.9595
Ave. abs. dev. in Z =	0.0035	0.0058	0.0051	0.0053
Max. % dev. in $(H-H_o)_T$ =	12.1024	14.8361	17.1674	17.1674
Max. abs. dev. in $(H-H_o)_T$ =	7.0811	3.8905	2.0000	2.0000
Ave. % dev. in $(H-H_o)_T$ =	5.1321	6.2422	6.6384	6.6097
Ave. abs. dev. in $(H-H_o)_T$ =	1.6915	1.5107	1.4681	1.4746

1 - Least Squares

2 - Min. max. abs. dev. in Z

3 - Min. max. abs. dev. in Z, subject to;

   Max. abs. dev. in $(H - H_o)_T \leq 2.0$ BTU/lb.

4 - Min. max. % dev. in Z subject to;

   Max. abs. dev. in $(H - H_o)_T \leq 2.0$ BTU/lb.

The B-W-R equation is difficult to fit because it con-
tains a non-linear exponential term. This necessitates the
use of a trial and error procedure to solve for the optimum
γ value.

To obtain optimum γ values for the various fitting
criteria, a trial and error search procedure was used. A
plot of fitting error versus γ was made to obtain the optimum
γ. A final solution was then made using the optimum γ value.

Fitting criteria 2, 3 and 4 required use of the linear
programming method of data fitting. The computer programs
required for this method are given in Appendix B and C, along
with an explanation of their usage.

$Z = \phi(P,T)$ FORMS

Equations of state of the form $Z = \phi(P,T)$ or $V = \phi(P,T)$ have one restriction. They may only be applied to a single phase region, since the function would otherwise have to be dual valued at pressures and temperatures along the vapor pressure curve. The $Z = \phi(P,T)$ form, however, has some features which make it attractive for engineering application.

In almost all engineering applications, the measured or given variables are pressure and temperature; thus, an equation of the form $V = \phi(P,T)$ can be solved explicitly. Equations of the form $P = \phi(V,T)$ require iterative solutions for volume. In terms of calculational efficiency, it is preferable to have a fairly complex form $V = \phi(P,T)$, rather than some simpler form $P = \phi(V,T)$. This, of course, assumes that the same degree of accuracy is obtainable with both equation forms. Furthermore, the derived thermodynamic properties most useful to engineers are defined as functions of P and T. As a result, equations of the form $V = \phi(P,T)$ give simpler expressions for such quantities as $(H - H_o)_T$, $(S - S_o)_T$, $(C_p - C_{p_o})_T$ and $\ln (f/P)$.

The thermodynamic quantities can be expressed as functions of V and T, but the functions become complicated and require an intermediate step in calculating. The given variables are generally P and T, requiring an iterative solution of the equation of state for V before any of the thermodynamic pro-

perties can be calculated.

Eight equations of the form $Z = \phi(P,T)$ were fitted to propane P-V-T data using minimization of the maximum absolute deviation in Z as the fitting criterion. The equation forms fitted contained from six to twenty terms. However, the accuracy of fit obtained with the equations tested did not approach anywhere near the accuracy of fit obtained using the B-W-R equation.

The investigation indicated that equations of the form $Z = \phi(P,T)$ may require forty or more terms in order to approach the accuracy obtainable with the B-W-R equation. The investigation was carried out using propane P-V-T data limited to pressures of two thousand psia. To make an equation of the form $Z = \phi(P,T)$ applicable to pressures of ten thousand psia would require many more terms. Thus, it was concluded, that equations of the form $Z = \phi(P,T)$ would be far too complex. Any advantage gained by an explicit form of equation would be lost due to the highly complex nature of the required function.

The following results are a summary of the various $Z = \phi(P,T)$ equations fitted. The data fitted allows direct comparison of fitting accuracy with the results presented for the B-W-R equation.

Analysis of Various Forms of $Z = \phi(P,T)$.

Data:

Propane vapor(6), 237 points.

P: 14.696⟶2057.44 psia

T: 545.67⟶1096.76 °R

1) Equation: (18 terms)

$$Z = 1.0 + A_1 \frac{P}{T} + A_2 \frac{P}{T^2} + A_3 \frac{P}{T^3} + A_4 \frac{P}{T^4} + A_5 \frac{P}{T^5} + A_6 \frac{P}{T^6}$$

$$+ B_1 \frac{P^2}{T} + B_2 \frac{P^2}{T^2} + B_3 \frac{P^2}{T^3} + B_4 \frac{P^2}{T^4} + B_5 \frac{P^2}{T^5} + B_6 \frac{P^2}{T^6}$$

$$+ C_1 \frac{P^3}{T} + C_2 \frac{P^3}{T^2} + C_3 \frac{P^3}{T^3} + C_4 \frac{P^3}{T^4} + C_5 \frac{P^3}{T^5} + C_6 \frac{P^3}{T^6}$$

Maximum absolute error in Z = 0.09624

2) Equation: (20 terms)

$$Z = 1.0 + A_1 \frac{P}{T} + A_2 \frac{P^2}{T} + A_3 \frac{P^3}{T} + A_4 \frac{P^4}{T} + A_5 \frac{P^5}{T} + A_6 \frac{P^6}{T}$$

$$+ A_7 \frac{P^7}{T} + A_8 \frac{P^8}{T} + B_1 \frac{P}{T^2} + B_2 \frac{P^2}{T^2} + B_3 \frac{P^3}{T^2} + B_4 \frac{P^4}{T^2}$$

$$+ B_5 \frac{P^5}{T^2} + B_6 \frac{P^6}{T^2} + B_7 \frac{P^7}{T^2} + B_8 \frac{P^8}{T^2} + C_1 \frac{P}{T^3} + C_2 \frac{P^2}{T^3}$$

$$+ C_3 \frac{P^3}{T^3} + C_4 \frac{P^4}{T^3}$$

Maximum absolute error in Z = 0.06822

3) Equation: (7 terms)

$$Z \;=\; 1.0 + A_1 \frac{P}{RT} + A_2 \frac{P}{R} + A_3 \frac{P}{RT^3} + A_4 \frac{P^2}{RT}$$

$$+ A_5 \frac{P^2}{R} + A_6 \frac{P^2}{RT^3} + A_7 \frac{P^3}{RT^3}$$

Maximum absolute error in Z = 0.1426

4) Equation: (12 terms)

$$Z \;=\; 1.0 + A_1 \frac{P}{RT} + A_2 \frac{P}{RT^2} + A_3 \frac{P}{RT^3} + A_4 \frac{P}{RT^4}$$

$$+ A_5 \frac{P}{RT^9} + B_1 \frac{P^2}{RT} + B_2 \frac{P^2}{RT^3} + B_3 \frac{P^2}{RT^9}$$

$$+ C_1 \frac{P^3}{RT} + C_2 \frac{P^3}{RT^3} + D_1 \frac{P^4}{RT^3} + E_1 \frac{P^5}{RT}$$

Maximum absolute error in Z = 0.09965

5) Equation: (11 terms)

$$Z \;=\; 1.0 + A_1 \frac{P}{R} + A_2 \frac{P}{RT} + A_3 \frac{P}{RT^2} + B_1 \frac{P^2}{R}$$

$$+ B_2 \frac{P^2}{RT} + B_3 \frac{P^2}{RT^3} + C_1 \frac{P^3}{RT} + C_2 \frac{P^3}{RT^3}$$

$$+ D_1 \frac{P^4}{R} + D_2 \frac{P^4}{RT^3} + E_1 \frac{P^5}{RT}$$

Maximum absolute error in Z = 0.09434

6) Equation: (15 terms)

$$Z = 1.0 + A_1 \frac{P}{R} + A_2 \frac{P}{RT} + A_3 \frac{P}{RT^3} + B_1 \frac{P^2}{R}$$

$$+ B_2 \frac{P^2}{RT} + B_3 \frac{P^2}{RT^3} + C_1 \frac{P^3}{R} + C_2 \frac{P^3}{RT}$$

$$+ C_3 \frac{P^3}{RT^3} + D_1 \frac{P^4}{R} + D_2 \frac{P^4}{RT} + D_3 \frac{P^4}{RT^3}$$

$$+ E_1 \frac{P^5}{R} + E_2 \frac{P^5}{RT} + E_3 \frac{P^5}{RT^3}$$

Maximum absolute error in Z = 0.09294

7) Equation: (6 terms)

$$Z = 1.0 + A_1 \frac{P}{R} + A_2 \frac{P}{RT} + B_1 \frac{P^2}{R} + B_2 \frac{P^2}{RT}$$

$$+ C_1 \frac{P^3}{RT} + D_1 \frac{P^4}{R}$$

Maximum absolute error in Z = 0.1125

8) Equation: (8 terms)

$$Z = 1.0 + A_1 \frac{P}{RT} + A_2 \frac{P}{R} + A_3 \frac{P}{RT^3} + B_1 \frac{P^2}{RT} + B_2 \frac{P^2}{R}$$

$$+ C_1 \frac{P^5}{RT} + D_1 P^2 \frac{e^{-\gamma/P^2}}{RT^3} + D_2 \frac{P^4 e^{-\gamma/P^2}}{RT^3}$$

Optimum $\gamma = 10.0$

Maximum absolute error in Z = 0.1358

<u>Z = φ(V,T) FORMS</u>

In the search for a better equation of state than the
B-W-R equation, the equation of state proposed by Martin and
Hou(15,16) was chosen as a starting point. The reasons for
this choice were:

1. The equation is easily expanded to include as many terms
    as desired.

2. Extensive physical argument is given for the form of the
    equation by Martin and Hou.

3. The equation is calculationally more efficient than the
    B-W-R equation. Exponential terms in the equation require
    evaluation of only one exponential quantity at a given
    temperature. Thus, the exponential quantity is excluded
    from iterative solutions of the equation for volume.

A preliminary investigation of the Martin-Hou equa-
tion in its original form was undertaken in order to determine
the ability of the equation to fit the P-V-T data for propane.
Results of this investigation are as follows:

<u>Preliminary Investigation of the Martin-Hou Equation</u>

Data:

Propane vapor(6), 237 points.

P: 14.696 ⟶ 2057.44 psia

T: 545.67 ⟶ 1096.76 °R

1) Original Equation: (8 terms)

$$b = 0.714598 \ (15)$$

$$Z = \frac{V}{(V-b)} + \frac{A_1 V}{RT(V-b)^2} + \frac{A_2 V}{RT(V-b)^3} + \frac{A_3 V}{RT(V-b)^4}$$

$$+ \frac{B_1 V}{R(V-b)^2} + \frac{B_2 V}{R(V-b)^3} + \frac{B_4 V}{R(V-b)^5}$$

$$+ \frac{C_1 V \, e^{-5.475 T_R}}{RT(V-b)^2} + \frac{C_2 V \, e^{-5.475 T_R}}{RT(V-b)^3}$$

Maximum absolute error in Z = 0.01524

2) Original Equation: suggested exponential term added;

$$b = 0.714598 \ (15)$$

$$Z = \frac{V}{(V-b)} + \frac{A_1 V}{RT(V-b)^2} + \frac{A_2 V}{RT(V-b)^3} + \frac{A_3 V}{RT(V-b)^4}$$

$$+ \frac{B_1 V}{R(V-b)^2} + \frac{B_2 V}{R(V-b)^3} + \frac{B_4 V}{RT(V-b)^5}$$

$$+ \frac{C_1 V \, e^{-5.475 T_R}}{RT(V-b)^2} + \frac{C_2 V \, e^{-5.475 T_R}}{(V-b)^3}$$

$$+ \frac{C_4 V \, e^{-5.475 T_R}}{(V-b)^5}$$

Maximum absolute error in Z = 0.01300

These results indicate that the original Martin-Hou
equation is comparable in accuracy of fit to the B-W-R equation.

The original Martin-Hou equation can be written in
the form:

$$Z = \frac{V}{(V-b)} + \frac{V}{RT} \sum_{i=1}^{n} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V-b)^{i+1}}$$

This, of course, is an expansion in $1/(V-b)^m$. In order to
determine the best expansion form, twelve term expansions of
the equation in $1/(V)^m$, $1/(V-b)^m$ and $1/(V+b)^m$ were made with
the following results.

Data:

      Propane(6) in the vapor region

1) $$Z = \frac{V}{(V-b)} + \frac{V}{RT} \sum_{i=1}^{4} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V-b)^{i+1}}$$

      $b = 0.714598$ (15)

Maximum absolute error in Z = 0.01212

2) $$Z = 1.0 + \frac{1}{RT} \sum_{i=1}^{4} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V)^{i}}$$

Maximum absolute error in Z = 0.01122

3) $$Z = \frac{V}{(V+b)} + \frac{V}{RT} \sum_{i=1}^{4} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V+b)^{i+1}}$$

      $b = 0.714598$ (15)

Maximum absolute error in Z = 0.01951

The results indicate that for the vapor region, the best expansion of the Martin-Hou equation is

$$Z = 1.0 + \frac{1}{RT} \sum_{i=1}^{n} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V)^i}$$

Expansion of the equation in $1/V^m$ gives the best results for the vapor region. However, the expansion in $1/(V-b)^m$ ran a close second and it was postulated that this expansion might have merit for fitting both liquid and vapor regions. In order to check out this possibility, fifteen constant expansions of the equation in $1/V^m$ and $1/(V-b)^m$ were made with the following results.

Data:

　　　Propane(6), in the vapor and liquid regions.

1)　　$$Z = 1.0 + \frac{1}{RT} \sum_{i=1}^{5} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V)^i}$$

Maximum absolute error in Z = 0.09227

2)　　$$Z = \frac{V}{(V-b)} + \frac{V}{RT} \sum_{i=1}^{5} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V-b)^{i+1}}$$

　　　$b = 0.714598$ (15)

Maximum absolute error in Z = 0.2949

The results indicate that the best expansion of the Martin-Hou equation is, regardless of the region to be fitted,

of the form:

$$Z = 1.0 + \frac{1}{RT} \sum_{i=1}^{n} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V)^i}$$

In order to obtain a direct comparison of fitting accuracy for fitting the gas and gas-liquid regions, a fifteen constant expansion of the above form was fitted to the vapor region only.

Equation:

$$Z = 1.0 + \frac{V}{RT} \sum_{i=1}^{5} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V)^i}$$

1) Data:

Propane(6), in the vapor region including data along the vapor pressure curve.

Maximum absolute error in Z = 0.009177

2) Data:

Propane(6), in the vapor region, no vapor pressure data included.

Maximum absolute error in Z = 0.009170

A direct comparison of fitting accuracy can be made between these results and those shown previously for the fifteen constant expansion in $1/V^m$, fitted to the vapor and liquid regions. Comparison of the results reveals an order of magnitude loss of accuracy upon inclusion of the liquid region P-V-T data. There is, however, no appreciable loss of

accuracy when vapor pressure data are included in the equation fit.

It was concluded, that, because of the serious loss of accuracy created by fitting both phases with the same equation, the equation should be limited to the vapor phase. This does not seriously limit the usefulness of the equation, as it can always be tied to an equation for the liquid phase by making the vapor and liquid fugacities match along the vapor pressure curve.

The fact that fifteen terms were used in the equation has no real significance. The choice was made for computational reasons. In formulating an equation of state, one must reach a compromise between computational efficiency and fitting accuracy.

The best nine and twelve constant expansions of the equation are given for comparative purposes. These expansions were obtained by trying various nine and twelve term combinations of the terms in the fifteen constant expansion.

It is important to remember that the equation coefficients are not linearly independent, therefore, they will have very different values, depending upon the number of terms used. Thus, to obtain constants for the nine and twelve constant equations, the data must be fitted using these equations.
Data:

Propane(6) in the vapor region, including data along the vapor pressure curve.

1) 15 Constant equation

$$Z = 1.0 + \frac{1}{RT} \sum_{i=1}^{5} \frac{(A_i + B_i T + C_i e^{-5.475T_R})}{(V)^i}$$

Maximum absolute error in Z = 0.009177

2) Best 9 constants

$$A_1, A_2, A_3, B_1, B_2, B_3, C_1, C_2, C_5$$

Maximum absolute error in Z = 0.01126

3) Best 12 constants

$$A_1, A_2, A_3, A_5, B_1, B_2, B_3, B_5, C_1, C_2, C_3, C_5$$

Maximum absolute error in Z = 0.01072

An equation explicit in Z is generally not a very use-
ful form; therefore, the equation was rearranged so as to be
explicit in pressure. Fifteen and twenty-one term expansions
of the equation, explicit in pressure, were obtained and
fitted to the propane data. These results give an indication
of the pressure errors of the fit and at the same time show
that higher order expansions do give a significant improvement
in fitting accuracy.

Data:

Propane(6), in the vapor region including vapor

pressure data.

1) Equation: (15 terms)

$$P = \frac{RT}{V} + \sum_{i=1}^{5} \frac{(A_i + B_i T + C_i e^{-5.475 T_R})}{(V)^{i+1}}$$

Maximum absolute error in P = 29.10 psia

2) Equation: (21 terms)

$$P = \frac{RT}{V} + \sum_{i=1}^{7} \frac{(A_i + B_i T + C_i e^{-5.475 T_R})}{(V)^{i+1}}$$

Maximum absolute error in P = 23.68 psia

It was discovered from these results, that minimizing the maximum absolute deviation in pressure is not a very good fitting criterion. Some of the maximum deviations in pressure occurred at points on the vapor pressure curve, where pressures are relatively low, causing large percentage errors in pressure (10%) in this region.

Percentage deviations have more significance than absolute deviations when the function being fitted has a very large range of values. The pressure range of greatest interest runs from about ten to ten thousand psia; hence, minimization of the maximum absolute percentage deviation in pressure was chosen as the better fitting criterion. This fitting criterion was applied to the fifteen constant expansion of the equation with the following results.

Propane data(6), for the vapor region, including the vapor pressure data.

$$P = \frac{RT}{V} + \frac{A_1}{V^2} + \frac{A_2}{V^3} + \frac{A_3}{V^4} + \frac{A_4}{V^5} + \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V^2} + \frac{B_2 T}{V^3} + \frac{B_3 T}{V^4} + \frac{B_4 T}{V^5} + \frac{B_5 T}{V^6}$$

$$+ [\frac{C_1}{V^2} + \frac{C_2}{V^3} + \frac{C_3}{V^4} + \frac{C_4}{V^5} + \frac{C_5}{V^6}] \ e^{-5.475 T_R}$$

Maximum absolute percentage deviation in P = 2.0260%

Up to this point in the investigation of equation of state forms, the entire study was restricted to the fitting of propane P-V-T data. Restricting the investigation to one vapor was very useful for establishing the best form of equation, the best fitting criterion, and the range of application. Having established this much for propane, it was necessary to establish the usefulness of the equation for a wide variety of vapors.

To establish the general utility of the equation a detailed fit of eight different vapors was carried out. The eight vapors fitted were methane, propane, ethylene, benzene, carbon dioxide, hydrogen sulfide, nitrogen and argon. The results of these equation fits are as follows:

Equation:

$$P = \frac{RT}{V} + \frac{A_1}{V^2} + \frac{A_2}{V^3} + \frac{A_3}{V^4} + \frac{A_4}{V^5} + \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V^2} + \frac{B_2 T}{V^3} + \frac{B_3 T}{V^4} + \frac{B_4 T}{V^5} + \frac{B_5 T}{V^6}$$

$$+ [\frac{C_1}{V^2} + \frac{C_2}{V^3} + \frac{C_3}{V^4} + \frac{C_4}{V^5} + \frac{C_5}{V^6}]\, e^{-5.475 T_R}$$

Fitting criterion:

Minimize the maximum absolute percentage deviation in pressure

Range of application:

$T \geqslant T_c$; All pressures up to the highest pressure of
interest.

$T < T_c$; All pressures up to and including the vapor
pressure.

(1) Material: Methane

Equation Constants:

T_c = 343.19°R

A_1 = -0.67068028 x 10^4

A_2 = -0.13433947 x 10^5

A_3 = +0.26809945 x 10^5

A_4 = -0.19713974 x 10^5

A_5 = +0.48385398 x 10^4

B_1 = +0.64013752 x 10^1

$$B_2 = +0.23022082 \times 10^2$$

$$B_3 = -0.30632364 \times 10^2$$

$$B_4 = +0.18616297 \times 10^2$$

$$B_5 = -0.11969532 \times 10^1$$

$$C_1 = -0.79486746 \times 10^6$$

$$C_2 = +0.36788516 \times 10^7$$

$$C_3 = -0.57315354 \times 10^7$$

$$C_4 = +0.35269793 \times 10^7$$

$$C_5 = -0.72916887 \times 10^6$$

Molecular weight = 16.043

Units:

$$R = 10.73147 \ (psia)(ft^3/lb\text{-}mole)/°R$$

$$P = psia$$

$$T = °R$$

$$V = ft^3/lb\text{-}mole$$

Range of Data:

P : 14.696 $\longrightarrow$ 14696 psia(12)

T : 365.69 $\longrightarrow$ 851.69°R

(169 points)

Max. % error in P = 0.7648%

Max. abs. error in P = 112.39 psia

Ave. abs. % error in P = 0.3923%

Ave. abs. error in P = 17.86 psia

(2) Material: Propane

Equation Constants:

$$T_c \ = \ 666.0°R$$

$$A_1 \ = \ +0.15065950 \times 10^5$$

$$A_2 \ = \ -0.11126574 \times 10^7$$

$$A_3 \ = \ +0.79445232 \times 10^7$$

$$A_4 \ = \ -0.22610278 \times 10^8$$

$$A_5 \ = \ +0.21827919 \times 10^8$$

$$B_1 \ = \ -0.45698786 \times 10^2$$

$$B_2 \ = \ +0.14768928 \times 10^4$$

$$B_3 \ = \ -0.10247113 \times 10^5$$

$$B_4 \ = \ +0.28824875 \times 10^5$$

$$B_5 \ = \ -0.27506201 \times 10^5$$

$$C_1 \ = \ -0.27058287 \times 10^7$$

$$C_2 \ = \ +0.31838750 \times 10^8$$

$$C_3 \ = \ -0.21227985 \times 10^9$$

$$C_4 \ = \ +0.67206797 \times 10^9$$

$$C_5 \ = \ -0.72138224 \times 10^9$$

Molecular Weight = 44.097

Units:

$$R \ = \ 10.73147 \ (psia)(ft^3/lb\text{-}mole)/°R$$

$$P \ = \ psia$$

$$T \ = \ °R$$

$$V \ = \ ft^3/lb\text{-}mole$$

Range of Data:

P : 14.696 ⟶ 2057 psia(6)

T : 545.69 ⟶ 1096.78°R

(245 points)

Max. % error in P = 2.0263%

Max. abs. error in P = 41.69 psia

Ave. abs. % error in P = 1.0292%

Ave. abs. error in P = 10.33 psia

(3) Material: Ethylene

Equation Constants:

T_c = 508.79°R

A_1 = -0.22753538 x 10^5

A_2 = +0.79991381 x 10^5

A_3 = -0.26390817 x 10^6

A_4 = +0.28374683 x 10^6

A_5 = -0.94597719 x 10^5

B_1 = +0.26812945 x 10^2

B_2 = -0.14424227 x 10^3

B_3 = +0.47236436 x 10^3

B_4 = -0.49954036 x 10^3

B_5 = +0.17726410 x 10^3

C_1 = -0.59373207 x 10^6

C_2 = -0.17246599 x 10^7

C_3 = +0.13444364 x 10^8

C_4 = -0.18112673 x 10^8

C_5 = +0.68660545 x 10^7

Molecular weight = 28.054

Units:

R = 10.73147 (psia)(ft^3/lb-mole)/°R

P = psia

T = °R

V = ft^3/lb-mole

Range of Data:

P : 14.878 ⟶ 37196 psia(7)

T : 491.69 ⟶ 761.69°R

(231) points)

Max. % error in P = 2.3992%

Max. abs. error in P = 892.44 psia

Ave. Abs. % error in P = 1.3188%

Ave. abs. error in P = 90.68 psia

(4) Material: Benzene

Equation Constants:

T_c = 1012.79°R

A_1 = +0.81343905 x 10^5

A_2 = -0.38590771 x 10^7

A_3 = +0.42759643 x 10^8

A_4 = -0.26575865 x 10^9

A_5 = +0.62507683 x 10^9

B_1 = -0.11161890 x 10^3

B_2 = +0.35639773 x 10^4

B_3 = -0.38597862 x 10^5

$$B_4 = +0.23327206 \times 10^6$$

$$B_5 = -0.53642336 \times 10^6$$

$$C_1 = -0.47924205 \times 10^7$$

$$C_2 = +0.56489854 \times 10^8$$

$$C_3 = -0.64244265 \times 10^9$$

$$C_4 = +0.62202228 \times 10^{10}$$

$$C_5 = -0.18566092 \times 10^{11}$$

Molecular weight = 78.114

Units:

$$R = 10.73147 \ (psia)(ft^3/lb\text{-}mole)/°R$$

$$P = psia$$

$$T = °R$$

$$V = ft^3/lb\text{-}mole$$

Range of Data:

P : 375.6 ⟶ 930.4 psia(9)

T : 952.02 ⟶ 1134.32°R

(187 points)

Max. % error in P = 0.3865%

Max. abs. error in P = 3.60 psia

Ave. abs. % error in P = 0.1865%

Ave. abs. error in P = 1.27 psia

(5) Material: Carbon Dioxide

Equation Constants:

$$T_c = 547.56°R$$

$$A_1 = -0.26280181 \times 10^5$$

$$A_2 = +0.96207443 \times 10^5$$

$$A_3 = -0.21501424 \times 10^6$$

$$A_4 = +0.17530775 \times 10^6$$

$$A_5 = -0.47329448 \times 10^5$$

$$B_1 = +0.27269119 \times 10^2$$

$$B_2 = -0.12725418 \times 10^3$$

$$B_3 = +0.29627500 \times 10^3$$

$$B_4 = -0.24136579 \times 10^3$$

$$B_5 = +0.66861749 \times 10^2$$

$$C_1 = +0.92167559 \times 10^5$$

$$C_2 = -0.49328657 \times 10^7$$

$$C_3 = +0.14323348 \times 10^8$$

$$C_4 = -0.13172478 \times 10^8$$

$$C_5 = +0.38213556 \times 10^7$$

Molecular weight = 44.011

Units:

$$R = 10.73147 \ (psia)(ft^3/lb\text{-}mole)/°R$$

$$P = psia$$

$$T = °R$$

$$V = ft^3/lb\text{-}mole$$

Range of Data:

P : 7.35 ⟶ 44088 psia(7)

T : 401.69 ⟶ 761.69°R

(242 points)

Max. % error in P = 1.5957%

Max. abs. error in P = 703.52 psia

Ave. abs. % error in P = 0.5670%

Ave. abs. error in P = 50.26 psia

(6) Material: Hydrogen Sulfide

Equation Constants:

$$T_c = 672.4°R$$
$$A_1 = -0.17219137 \times 10^5$$
$$A_2 = -0.12356671 \times 10^6$$
$$A_3 = +0.53008304 \times 10^6$$
$$A_4 = -0.72407331 \times 10^6$$
$$A_5 = +0.31145722 \times 10^6$$
$$B_1 = -0.24436326 \times 10^1$$
$$B_2 = +0.24040259 \times 10^3$$
$$B_3 = -0.83492352 \times 10^3$$
$$B_4 = +0.10516778 \times 10^4$$
$$B_5 = -0.43005513 \times 10^3$$
$$C_1 = +0.29752710 \times 10^6$$
$$C_2 = -0.18326696 \times 10^7$$
$$C_3 = -0.11910975 \times 10^7$$
$$C_4 = +0.91815119 \times 10^7$$
$$C_5 = -0.61695012 \times 10^7$$

Molecular weight = 34.082

Units:

$$R = 10.73147 \text{ (psia)}(ft^3/lb\text{-mole})/°R$$

P = psia

T = °R

V = ft^3/lb-mole

Range of Data:

P : 14.696 ⟶ 10,000 psia(20)

T : 499.69 ⟶ 799.69°R

(202 points)

Max. % error in P = 4.6444%

Max. abs. error in P = 464.45 psia

Ave. abs. % error in P = 2.0817%

Ave. abs. error in P = 44.62 psia

(7) Material: Nitrogen

Equation Constants:

T_C = 226.8°R

A_1 = -0.67355560×10^4

A_2 = $+0.75599856 \times 10^4$

A_3 = -0.14046270×10^5

A_4 = $+0.12607564 \times 10^5$

A_5 = -0.40924410×10^4

B_1 = $+0.11494687 \times 10^2$

B_2 = -0.99447537×10^1

B_3 = $+0.27365071 \times 10^2$

B_4 = -0.24403024×10^2

B_5 = $+0.91193732 \times 10^1$

$$C_1 = -0.99546378 \times 10^5$$

$$C_2 = -0.21271695 \times 10^6$$

$$C_3 = +0.21250628 \times 10^7$$

$$C_4 = -0.41404779 \times 10^7$$

$$C_5 = +0.19459221 \times 10^7$$

Molecular weight = 28.016

Units:

$$R = 10.73147 \ (psia)(ft^3/lb\text{-}mole)/°R$$

$$P = psia$$

$$T = °R$$

$$V = ft^3/lb\text{-}mole$$

Range of Data:

$$P : 6.6 \longrightarrow 14741 \ psia(17)$$

$$T : 221.69 \longrightarrow 761.69°R$$

(109 points)

Max. % error in P = 0.5223%

Max. abs. error in P = 76.53 psia

Ave. abs. % error in P = 0.2591%

Ave. abs. error in P = 11.78 psia

(8) Material: Argon

Equation Constants:

$$T_c = 271.3°R$$

$$A_1 = -0.43563009 \times 10^4$$

$$A_2 = +0.50761453 \times 10^3$$

$$A_3 = -0.90829412 \times 10^4$$

$$A_4 = +0.11013453 \times 10^5$$

$$A_5 = -0.35006883 \times 10^4$$

$$B_1 = +0.79613487 \times 10^1$$

$$B_2 = -0.85922136 \times 10^1$$

$$B_3 = +0.34658412 \times 10^2$$

$$B_4 = -0.32599490 \times 10^2$$

$$B_5 = +0.98217947 \times 10^1$$

$$C_1 = -0.15747792 \times 10^6$$

$$C_2 = -0.44802253 \times 10^6$$

$$C_3 = +0.21020384 \times 10^7$$

$$C_4 = -0.20411990 \times 10^7$$

$$C_5 = +0.58566869 \times 10^6$$

Molecular weight = 39.944

Units:

$$R = 10.73147 \ (psia)(ft^3/lb\text{-}mole)/°R$$

$$P = psia$$

$$T = °R$$

$$V = ft^3/lb\text{-}mole$$

Range of Data:

$$P : 14.696 \longrightarrow 14696 \ psia(7)$$

$$T : 180.0 \longrightarrow 1080°R$$

Max. % error in P = 3.7363%

Max. abs. error in P = 549.1 psia

Ave. abs. % error in P = 1.5214%

Ave. abs. error in P = 47.23 psia

The fitting accuracy of the fifteen constant equation, indicated by the previous results, was very good considering the wide range of pressures and temperature covered. It is important to remember, however, that the proposed equation is empirical and, therefore, the accuracy of the equation is only guaranteed within the range of the variables fitted.

There is one further modification of the equation which could be made to improve the P-V-T fit of a particular vapor. The exponential term in the equation could be expressed in the form e^{-BT_R}, with B being another constant to be determined for a particular vapor. This seemingly minor modification, however, makes the equation non-linear, requiring an iterative search procedure for obtaining the optimum B value. Since this study was aimed primarily at establishing the best equation form, the approach taken by Martin and Hou was adhered to.

Martin and Hou suggested that one value of B (5.475) is applicable to all vapors and this was their primary reason for using the exponential temperature term in their equation. They did considerable work to establish the best value of B(5.475); hence, this value was used in all work done on the equation in this thesis.

The proposed equation of state gives an improved representation of the volumetric behavior of pure vapors, but, it suffers from a deficiency common to all equations of the form $P = \phi(V,T)$. Equations of this form can predict pressures

to an accuracy predicted by the fitting procedure. Calcula-
tion of volume values, however, is an entirely different story.

The accuracy of calculated volumes is dependent upon
$(\frac{\partial P}{\partial T})_V$. In regions where $|(\frac{\partial P}{\partial T})_V|$ is less than 0.5, calculated
volumes will be less accurate than calculated pressures, where
$|(\frac{\partial P}{\partial T})_V|$ is greater than 0.5, calculated volumes will be more
accurate than calculated pressures. This means that in most
of the vapor region, calculated volumes will be quite accur-
ate. In the vicinity of the critical point, however, such is
not the case. In this region $|(\frac{\partial P}{\partial T})_V|$ is approaching zero or
very small values. This means that volumes calculated in the
region of the critical point will be in error by a factor of
several times the predicted error in pressure. For this reason,
equations of state which are explicit in pressure are not re-
commended for calculating volumes in the region of the critical
point.

Having established the proposed equation's ability to
predict accurate volumetric relationships in all but the critical
region, work was undertaken to establish the equation's ability
to predict accurate derived thermodynamic properties.

GENERAL CHARACTERISTICS OF APPROXIMATING FUNCTIONS

Much information about the accuracy of various derived thermodynamic properties can be gained by looking at some general characteristics of approximating functions.

Approximating functions are exactly what the name implies. They are an approximation to some exact function. This means that there will be some error associated with each point on the functional curve obtained by fitting the approximating function to the data. As a result of the associated errors, approximating functions are cyclic in nature in that they follow the true function but cycle above and below it. As the number of terms in the approximating function is increased, the amplitude of the deviations decreases, but at the same time the frequency of cycling increases.

The cyclic nature of the approximating function causes large deviations in the predicted derivative values. Maximum deviations in the derivatives occur where the approximating function has zero deviation (crosses the actual function). Integrals of the approximating function will usually be very accurate due to the partial cancellation of positive and negative deviations.

Derived thermodynamic properties depend upon integration and differentiation of an approximating function (equation of state). If we look at the mathematical processes that each derived thermodynamic property is dependent upon, we can obtain some idea of the relative accuracy of the calculated values.

RELATIVE ACCURACY OF CALCULATED THERMODYNAMIC PROPERTIES

1) $$(\Delta A)_T = -\int P \, dv$$

$$(\Delta F)_T = (\Delta A)_T + \Delta (PV)_T$$

$$\ln \left(\frac{f}{f_O}\right) = \frac{(\Delta F)_T}{RT}$$

The accuracy of these quantities will be greater than the accuracy of calculated pressures since all of the quantities are dependent upon the process of integration.

2) $$(\Delta E)_T = \int \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

$$(\Delta H)_T = (\Delta E)_T + \Delta (PV)_T$$

$$(\Delta S)_T = \int \left(\frac{\partial P}{\partial T}\right)_V dV$$

These quantities will be less accurate than calculated pressures. They are partially dependent upon derivatives of the pressure function. Some improvement in accuracy is attained by integration of the derivatives but not enough to overcome the inaccuracy of the derivatives themselves.

3) $$\mu = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{Cp}\left(\frac{\partial H}{\partial P}\right)_T = \frac{1}{Cp}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

Joule-Thompson coefficients will be quite inaccurate because of their direct dependency upon derivatives.

4) $(C_p - C_{p_o})_T = -T \int (\frac{\partial^2 V}{\partial T^2})_p \, dP$

Errors in the functional relationship are magnified to a very great extent when second derivatives of the function are taken. As a result, calculated values of C_p at elevated pressure will be unreliable.

IMPROVING THE PREDICTION OF THERMODYNAMIC PROPERTIES

One of the primary reasons for developing equations
of state is their usefulness in calculating derived thermo-
dynamic properties. Having an equation of state allows the
development of explicit relationships for the important derived
thermodynamic properties. The most important derived properties
from an engineering standpoint are $(H - H_o)_T$, $(S - S_o)_T$ and
f/P. Expressions for all of these are easily derived from an
equation of state.

Most of the derived thermodynamic property values re-
ported in the literature have been obtained by graphical inte-
gration and differentiation of experimental P-V-T data. Values
obtained in this manner are highly dependent upon the accuracy
of the P-V-T data and the graphical techniques employed in
their calculation. In order to exclude any dependency upon
calculational techniques, it was decided that directly measured
experimental values for the thermodynamic properties would be
used for determining the accuracy of values calculated from an
equation of state.

Of the three important derived properties, $(H - H_o)_T$
is the only one for which there are any experimentally deter-
mined data available. As a result, the study of derived thermo-
dynamic properties was restricted to enthalpy departure.

A method of improving the ability of equations of state
to predict thermodynamic properties was developed and applied

specifically to the improvement of $(H - H_o)_T$ predictions. The
method was first applied to the B-W-R equation in order to
evaluate its usefulness. Results of this application were
presented in the previous discussion of the B-W-R equation and
they justify the further application of the method.

The method used for improving enthalpy departure pre-
dictions includes enthalpy departure data into the equation
of state fitting procedure and can be formulated as a linear
programming problem in the following manner:

Minimize the maximum absolute deviations

λ and β, subject to

$$\left| P - f(V,T) \right| \, i \leqslant \lambda$$

$$\left| (H - H_o)_T - g(V,T) \right| \, i \leqslant \beta$$

i refers to a particular data point.

The set of constraint equations formulated cannot be
solved directly, as linear programming allows the optimization
of only one objective function. The formulated problem con-
tains two objective functions, λ and β. There are two means
of overcoming this difficulty.

1) Let $\beta = \omega\lambda$, where ω is some arbitrary weighting factor.

2) Let $\beta = K$, where K is some arbitrary constant.

Caution must be exercised when using method (2). If
the constant K specified is too small, there may not be a
solution to the linear programming problem. In actual applica-

tion, the computer program given in Appendix C for solution of this problem, will print "unbounded solution" and cease calculating.

The most useful formulation of the linear programming problem for fitting equations of state was found to be

$$\left| \frac{P - f(V,T)}{P} \right|_i < \lambda$$

$$\left| (H - H_o)_T - g(V,T) \right|_i < K$$

i refers to a particular data point.

Objective: minimize λ (maximum % error in P).

Specify K, the maximum allowable error in $(H - H_o)_T$.

Computer programs required for the solution of this linear programming problem are given in Appendix C, along with an explanation of their usage.

Improvement of the enthalpy departure predictions was carried out on the proposed fifteen constant equation of state. Experimental enthalpy departures could only be found for methane, propane and benzene; thus, the fitting procedure was only applied to these vapors. Results of the fitting procedure are as follows:

Equation of State:

$$P = \frac{RT}{V} + \frac{A_1}{V^2} + \frac{A_2}{V^3} + \frac{A_3}{V^4} + \frac{A_4}{V^5} + \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V^2} + \frac{B_2 T}{V^3} + \frac{B_3 T}{V^4} + \frac{B_4 T}{V^5} + \frac{B_5 T}{V^6}$$

$$+ [\frac{C_1}{V^2} + \frac{C_2}{V^3} + \frac{C_3}{V^4} + \frac{C_4}{V^5} + \frac{C_5}{V^6}] \ e^{-5.475 T_R}$$

Enthalpy Departure Equation:

$$(H - H_o)_T = J \ [2 \ \frac{A_1}{V} + \frac{3}{2} \frac{A_2}{V^2} + \frac{4}{3} \frac{A_3}{V^3} + \frac{5}{4} \frac{A_4}{V^4} + \frac{6}{5} \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V} + \frac{B_2 T}{V^2} + \frac{B_3 T}{V^3} + \frac{B_4 T}{V^4} + \frac{B_5 T}{V^5}$$

$$+ (\frac{C_1 (2 + 5.475 T_R)}{V} + \frac{C_2 (3 + 5.475 T_R)}{V^2}$$

$$+ \frac{C_3 (4 + 5.475 T_R)}{V^3} + \frac{C_4 (5 + 5.475 T_R)}{V^4}$$

$$+ \frac{C_5 (6 + 5.475 T_R)}{V^5}) \ e^{-5.475 T_R}]$$

J - units conversion from units of PV to BTU/lb.

Fitting Criterion:

Minimize the maximum percentage error in P subject

to the maximum absolute error in $(H - H_o)_T \leq 2.0$ BTU/lb.

(1) Material: Methane

Equation Constants:

$$T_C = 343.19°R$$

$$A_1 = -0.10485025 \times 10^5$$

$$A_2 = +0.50240222 \times 10^4$$

$$A_3 = -0.48803061 \times 10^4$$

$$A_4 = +0.32307928 \times 10^4$$

$$A_5 = -0.10977803 \times 10^4$$

$$B_1 = +0.12119481 \times 10^2$$

$$B_2 = -0.45553829 \times 10^1$$

$$B_3 = +0.16332147 \times 10^2$$

$$B_4 = -0.15146344 \times 10^2$$

$$B_5 = +0.74635761 \times 10^1$$

$$C_1 = -0.21888554 \times 10^6$$

$$C_2 = +0.82097618 \times 10^6$$

$$C_3 = -0.77795798 \times 10^6$$

$$C_4 = -0.89290670 \times 10^5$$

$$C_5 = +0.21571796 \times 10^6$$

Molecular weight = 16.043

Units:

$$R = 10.73147 \ (psia)(ft^3/lb\text{-mole})/°R$$

$$J = 144.0/(mol.\ wt.\ \times\ 778.173) \ \frac{(in^2)(lb\text{-mole})(BTU)}{(ft^2)(lb)(ft\text{-}lb_f)}$$

$$P = psia \qquad V = ft^3/lb\text{-mole}$$

$$T = °R \qquad (H-H_o)_T = BTU/lb.$$

Range of Data:

      (a)   PVT data :   P : 14.696 $\longrightarrow$ 14696 psia(12)

         (169 points) T : 365.69 $\longrightarrow$ 851.69°R

      (b) $(H-H_O)_T$ data :   P : 600 $\longrightarrow$ 2000 psia(11)

         (20 points)   T : 399.69 $\longrightarrow$ 489.69°R

Max. % error in P = 0.7672%

Max. abs. error in P = 112.74 psia

Ave. abs.% error in P = 0.3692%

Ave. abs. error in P = 16.92 psia

Max. % error in $(H-H_O)_T$ = 5.0085%

Max. abs. error in $(H-H_O)_T$ = 2.00 BTU/lb.

Ave. abs.% error in $(H-H_O)_T$ = 2.6900%

Ave. abs. error in $(H-H_O)_T$ = 1.17 BTU/lb.

(2) Material: Propane

Equation Constants:

$$T_C = 666.0°R$$
$$A_1 = -0.25705848 \times 10^5$$
$$A_2 = -0.46766287 \times 10^6$$
$$A_3 = +0.41155780 \times 10^7$$
$$A_4 = -0.13127352 \times 10^8$$
$$A_5 = +0.13617211 \times 10^8$$
$$B_1 = +0.63466624 \times 10^1$$
$$B_2 = +0.62921939 \times 10^3$$
$$B_3 = -0.52240027 \times 10^4$$
$$B_4 = +0.16491636 \times 10^5$$
$$B_5 = -0.16918478 \times 10^5$$

$$C_1 = -0.16189794 \times 10^7$$

$$C_2 = +0.16956579 \times 10^8$$

$$C_3 = -0.11384937 \times 10^9$$

$$C_4 = +0.39697617 \times 10^9$$

$$C_5 = -0.46090494 \times 10^9$$

Molecular weight = 44.097

Units:

$$R = 10.73147 \ (\text{psia})(\text{ft}^3/\text{lb-mole})/°R$$

$$J = 144.0/(\text{mol.wt.} \times 778.173) \ \frac{(\text{in}^2)(\text{lb-mole})(\text{BTU})}{(\text{ft}^2)(\text{lb})(\text{ft-lb}_f)}$$

$$P = \text{psia} \qquad\qquad V = \text{ft}^3/\text{lb-mole}$$

$$T = °R \qquad\qquad (H-H_o)_T = \text{BTU/lb.}$$

Range of Data:

(a) PVT data   P : 14.696 $\longrightarrow$ 2057 psia(6)

    (245 points)   T : 545.69 $\longrightarrow$ 1096.78°R

(b) $(H-H_o)_T$ data   P : 200 $\longrightarrow$ 1000 psia(21)

    (11 points)   T : 659.63 $\longrightarrow$ 859.63°R

Max. % error in P = 2.1379%

Max. abs. error in P = 43.99 psia

Ave.abs.% error in P = 1.0220%

Ave. abs. error in P = 10.72 psia

Max. % error in $(H-H_o)_T$ = 16.2192%

Max.abs. error in $(H-H_o)_T$ = 2.00 BTU/lb

Ave.abs.% error in $(H-H_o)_T$ = 6.2454%

Ave. abs. error in $(H-H_o)_T$ = 1.36 BTU/lb

(3) Material: Benzene

Equation Constants:

$$T_C = 1012.79°R$$

$$A_1 = -0.14282083 \times 10^6$$

$$A_2 = +0.37980274 \times 10^7$$

$$A_3 = -0.73156804 \times 10^8$$

$$A_4 = +0.47849122 \times 10^9$$

$$A_5 = -0.96045465 \times 10^9$$

$$B_1 = +0.92470515 \times 10^2$$

$$B_2 = -0.33672543 \times 10^4$$

$$B_3 = +0.63698605 \times 10^5$$

$$B_4 = -0.41041176 \times 10^6$$

$$B_5 = +0.81809824 \times 10^6$$

$$C_1 = -0.16911234 \times 10^6$$

$$C_2 = -0.11270206 \times 10^9$$

$$C_3 = +0.24748603 \times 10^{10}$$

$$C_4 = -0.16527034 \times 10^{11}$$

$$C_5 = +0.33384717 \times 10^{11}$$

Molecular Weight = 78.114

Units:

$$R = 10.73147 \text{ (psia)(ft}^3/\text{lb-mole})/°R$$

$$J = 144.0/(\text{mol.wt.} \times 778.173) \; \frac{(\text{in}^2)(\text{lb-mole})(\text{BTU})}{(\text{ft}^3)(\text{lb})(\text{ft-lb}_f)}$$

$$P = \text{psia} \qquad V = \text{ft}^3/\text{lb-mole}$$

$$T = °R \qquad (H-H_o)_T = \text{BTU/lb}$$

Range of Data:

       (a) PVT data   P : 375.6 $\longrightarrow$ 930.4 psia(9)

         (187 points)   T : 952.02 $\longrightarrow$ 1134.32°R

       (b) $(H-H_o)_T$ data   P : 429.42 $\longrightarrow$ 929.69 psia(8)

         (8 points)   T : 1012.79 $\longrightarrow$ 1215.35°R

Max. % error in P = 0.5717%

Max. abs. error in P = 5.32 psia

Ave. abs. % error in P = 0.2814%

Ave. abs. error in P = 1.90 psia

Max. % error in $(H-H_o)_T$ = 17.0068%

Max. abs. error in $(H-H_o)_T$ = 2.00 BTU/lb

Ave. abs. % error in $(H-H_o)_T$ = 5.4083%

Ave. abs. error in $(H-H_o)_T$ = 1.50 BTU/lb.

The results of the improved enthalpy departure fitting procedure have little meaning without some means of comparing the results with the enthalpy departure predicted by the equation of state when fitted with just P-V-T data. To make a comparison of the results, programs were set up to calculate enthalpy departures using equation constants from the two fitting procedures.

Two methods of calculating enthalpy departures were employed. For comparison of the data fitting procedures results obtained by specifying V and T are best. Results were also obtained by specifying P and T. These results have greater practical interest as P and T are the variables which

are usually specified. Examples of the computer programs
used for both calculational procedures are given in Appendix
D.

(1) Material: Methane

Calculation of Enthalpy Departures (20 points):

(a) Given P and T, calculate V and $(H-H_o)_T$.

	Constraint:	
	A	B
Max. % error in V =	3.5571%	3.9477
Max. abs. error in V =	0.0713 ft^3/lb-mole	0.0533
Ave.abs. % error in V =	0.9038%	0.7657
Ave. abs. error in V =	0.0310 ft^3/lb-mole	0.0210
Max. % error in $(H-H_o)_T$ =	16.8890%	5.7782
Max. abs. error in $(H-H_o)_T$ =	5.8841 BTU/lb	1.9529
Ave. abs. % error in $(H-H_o)_T$ =	4.5577%	2.9461
Ave. abs. error in $(H-H_o)_T$ =	2.2317 BTU/lb	1.2688

(b) Given V and T, calculate P and $(H-H_o)_T$.

	Constraint:	
	A	B
Max. % error in P =	3.3190%	3.6189
Max. abs. error in P =	54.5964 psia	54.5127
Ave.abs. % error in P =	0.8359%	0.7153
Ave. abs. error in P =	11.0164 psia	10.2640

Max % error in $(H-H_o)_T$ = 17.2982%   5.0085

Max. abs.error in $(H-H_o)_T$ = 7.6532 BTU/lb   2.0000

Ave.abs.% error in $(H-H_o)_T$ = 4.7163%   2.6900

Ave. abs. error in $(H-H_o)_T$ = 2.4741 BTU/lb   1.1662

Constraints:

    A - PVT fit; minimize the maximum percentage error

        in P.

    B - PVT fit; minimize the maximum percentage error

        in P,subject to,the maximum absolute error in

        $(H-H_o)_T \leq 2.0$ BTU/lb.

(2) Material: Propane

Calculation of Enthalpy Departures(11 points):

    (a) Given P and T,calculate V and $(H-H_o)_T$.

Constraint:

	A	B
Max. % error in V =	8.4277%	8.0664
Max. abs. error in V =	0.5523 ft^3/lb-mole	0.5286
Ave.abs. % error in V =	1.7192%	1.4979
Ave. abs. error in V =	0.1823 ft^3/lb-mole	0.1469
Max. % error in $(H-H_o)_T$ =	48.5140%	15.3019
Max. abs. error in $(H-H_o)_T$ =	8.4032 BTU/lb	2.5586
Ave.abs. % error in $(H-H_o)_T$ =	19.7735%	6.3195
Ave. abs. error in $(H-H_o)_T$ =	4.4893 BTU/lb	1.3565

(b) Given V and T,calculate P and $(H-H_o)_T$.

<div align="center">Constraint:</div>

	A	B
Max. % error in P =	2.2995%	2.3991
Max. abs. error in P =	19.5796 psia	13.4348
Ave.abs. % error in P =	0.9391%	0.7440
Ave. abs. error in P =	5.9783 psia	4.5741
Max. % error in $(H-H_o)_T$ =	48.8229%	16.2192
Max. abs. error in $(H-H_o)_T$ =	8.0130 BTU/lb	2.0000
Ave.abs. % error in $(H-H_o)_T$ =	19.1293%	6.2454
Ave. abs. error in $(H-H_o)_T$ =	4.1812 BTU/lb	1.3614

Constraints:

     A - PVT fit; minimize the maximum percentage error in P.

     B - PVT fit; minimize the maximum percentage error in P, subject to,the maximum absolute error in $(H-H_o)_T \leq 2.0$ BTU/lb.

(3) Material: Benzene

Calculation of Enthalpy Departures (8 points):

(a) Given P and T,calculate V and $(H-H_o)_T$.

<div align="center">Constraint:</div>

	A	B
Max. % error in V =	0.0024%	4.4733
Max. abs. error in V =	0.0003 ft^3/lb-mole	0.7229
Ave.abs. % error in V =	0.000305%	1.4762
Ave. abs. error in V =	0.000031 ft^3/lb-mole	0.1833

Max. % error in $(H-H_o)_T$ = 51.9400%   14.672

Max. abs. error in $(H-H_o)_T$ = 14.1720 BTU/lb   7.0248

Ave.abs. % error in $(H-H_o)_T$ = 28.2720%   5.5060

Ave. abs. error in $(H-H_o)_T$ = 8.6639 BTU/lb   1.4762

    (b)   Given V and T, calculate P and $(H-H_o)_T$.

Constraint:

	A	B
Max. % error in P =	0.0019%	22.4251
Max. abs. error in P =	0.0181 psia	208.4839
Ave.abs. % error in P =	0.0010%	3.4630
Ave. abs. error in P =	0.0072 psia	29.7753
Max. % error in $(H-H_o)_T$ =	51.9400%	17.0068
Max. abs. error in $(H-H_o)_T$ =	14.1714 BTU/lb	2.0000
Ave.abs. % error in $(H-H_o)_T$ =	28.2717%	1.5043
Ave. abs. error in $(H-H_o)_T$ =	8.6638 BTU/lb	5.4083

Constraints:

    A - PVT fit, minimize the maximum percentage error in P

    B - PVT fit, minimize the maximum percentage error in P subject to the maximum absolute error in $(H-H_o)_T \leq$ 2.0 BTU/lb.

The enthalpy departures, calculated from the proposed equation of state, using equation constants obtained by both fitting procedures, indicate the usefulness of including

enthalpy departure data in the fitting procedure. Very sub-
stantial improvements in calculated enthalpy departures can be
obtained with only a small loss in accuracy in predicted
volumetric behavior.

There are obvious discrepancies in the pressures predicted
by the equation of state using either set of equation constants.
The pressure discrepancies become evident when the calculated
maximum percentage errors in pressure are compared to the maxi-
mum errors predicted by the linear programming data fitting
procedures. The pressure discrepancies, however, occur only
at points in the enthalpy departure data sets.

The pressure discrepancies in the enthalpy departure
data sets are a result of errors in the volume values used.
The available experimental enthalpy departure data was re-
ported at fixed pressures and temperatures with no correspond-
ing volume values given. Unfortunately, the expression for
enthalpy departure, obtained from an equation of state expli-
cit in pressure, is a function of volume and temperature.

Volume values, used with the enthalpy departure data,
for propane and methane were obtained from the P-V-T data by
Lagrangian interpolation. Benzene volumes used were calcu-
lated from the proposed equation of state fitted to the
P-V-T data. Use of either of these methods for obtaining the
volume values results in some error in the volumes.

Small inconsistencies between the P-V-T and enthalpy
departure data do not disrupt the fitting procedure to any

great extent. This fact is borne out in the results obtained
by calculating enthalpy departures from the proposed equation
of state at given pressures and temperatures. The enthalpy
departures calculated in this manner, with equation constants
from the enthalpy constrained fitting procedure, retain their
improvement, even though volume errors are incorporated into
the calculated enthalpy departures.

The enthalpy data used for benzene was found to contain
serious errors. Evidence of the errors in these data is pre-
sented by Yarborough and Edmister(21). Inclusion of benzene
enthalpy departure data into the fitting procedure completely
disrupted the equation fit. The enthalpy departure constrained
fit for benzene is quite useless but does illustrate the need
for careful examination of the thermodynamic data to be in-
cluded into the fitting procedure.

To obtain completely consistent results, when includ-
ing thermodynamic data in the fitting procedure, the P-V-T
and thermodynamic data used must be a complete set. This
means that there must be a P-V-T data point for every thermo-
dynamic data point used in the fitting procedure. If data
of this type are used, the maximum errors in the calculated
properties will not exceed the maximum errors predicted by
the fitting procedure.

The accuracy of a particular property, however, is
only guaranteed over the range of variables for which data
for that property has been included in the fitting procedure.

CONCLUSIONS

The proposed fifteen constant modified version of the Martin-Hou equation of state is a very effective means of representing the P-V-T behavior of a wide variety of vapors. The form of the equation is such that it allows the use of more or less than fifteen constants, depending on the range of data to be fitted and the degree of accuracy desired. The fifteen constant form was chosen as a compromise between accuracy and calculational efficiency.

The proposed equation of state contains high powers in volume and, therefore, the method of linear programming data fitting should be used for fitting the equation. "Least squares" data fitting will result in an ill-conditioned set of equations when applied to this equation.

Pressure predictions of the proposed equation of state are quite accurate over the entire vapor region. The equation, however, will not predict accurate volumes in the critical region. This is a common failing of all equations of state which are explicit in pressure.

Volumes can be calculated, by iterative means, from the proposed equation of state more efficiently than from the B-W-R equation. The calculational efficiency of the proposed equation is due to the fact that the exponential quantities in the equation are not involved in iterative procedures required for calculating volumes.

Thermodynamic properties calculated from the proposed equation of state are no more accurate than those calculated from lower order equations of state. Improved thermodynamic properties, however, may be obtained by including accurate thermodynamic properties in the equation fitting procedure.

RECOMMENDATIONS

Further work is required to make the proposed equation of state more useful, since the primary objective of this investigation was to establish the basic form for an equation of state.

The equation of state presented is only applicable to the vapor phase; therefore, a complimentary equation of state for the liquid phase must be developed for a complete description of the volumetric behavior of pure fluids. An equation of state for the liquid phase could be made compatible with the vapor phase equation by use of the two constraint linear programming data fitting procedure. Pressures or fugacities at points on the vapor pressure curve could be used as the binding constraint for tying in the liquid phase equation.

The usefulness of, and method for, including thermodynamic properties in the data fitting procedure has been indicated. Application of this data fitting procedure is recommended whenever the equation of state may be used for the calculation of thermodynamic properties. Equations of state do not predict accurate thermodynamic properties when fitted exclusively to P-V-T data. This, of course, depends upon the particular thermodynamic property.

Development of some form of mixing rule for the equation is required to make it useful for predicting the volumetric behavior of mixtures.

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A P P E N D I X   A

PROPOSED EQUATION OF STATE

Use of this equation is only recommended for pure vapors within the range of P-V-T data used to obtain the equation constants. The equation, however, is not recommended for calculating volumes in the critical region.

The linear programming method of data fitting should be used for obtaining the equation coefficients. Minimizing of the maximum percentage deviation in pressure is the best fitting criterion in most instances.

1) $$P = \frac{RT}{V} + \frac{A_1}{V^2} + \frac{A_2}{V^3} + \frac{A_3}{V^4} + \frac{A_4}{V^5} + \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V^2} + \frac{B_2 T}{V^3} + \frac{B_3 T}{V^4} + \frac{B_4 T}{V^5} + \frac{B_5 T}{V^6}$$

$$+ [\frac{C_1}{V^2} + \frac{C_2}{V^3} + \frac{C_3}{V^4} + \frac{C_4}{V^5} + \frac{C_5}{V^6}] e^{-5.475 T_R}$$

2) $$Z = 1.0 + \frac{A_1}{RTV} + \frac{A_2}{RTV^2} + \frac{A_3}{RTV^3} + \frac{A_4}{RTV^4} + \frac{A_5}{RTV^5}$$

$$+ \frac{B_1}{RV} + \frac{B_2}{RV^2} + \frac{B_3}{RV^3} + \frac{B_4}{RV^4} + \frac{B_5}{RV^5}$$

$$+ [\frac{C_1}{RTV} + \frac{C_2}{RTV^3} + \frac{C_3}{RTV^3} + \frac{C_4}{RTV^4} + \frac{C_5}{RTV^5}] e^{-5.475 T_R}$$

3) $\quad (E - E_o)_T = \dfrac{A_1}{V} + \dfrac{A_2}{2V^2} + \dfrac{A_3}{2V^3} + \dfrac{A_4}{4V^4} + \dfrac{A_5}{5V^5}$

$\qquad + [\dfrac{C_1}{V} + \dfrac{C_2}{2V^2} + \dfrac{C_3}{3V^3} + \dfrac{C_4}{4V^4}$

$\qquad + \dfrac{C_5}{5V^5}] \, (1+5.475T_R) e^{-5.475T_R}$

$\qquad E_o \; = \;$ ideal gas internal energy.

4) $\quad (H - H_o)_T = \dfrac{2A_1}{V} + \dfrac{3}{2} \dfrac{A_2}{V^2} + \dfrac{4}{3} \dfrac{A_3}{V^3} + \dfrac{5}{4} \dfrac{A_4}{V^4}$

$\qquad + \dfrac{6}{5} \dfrac{A_5}{V^5} + \dfrac{B_1 T}{V} + \dfrac{B_2 T}{V^2} + \dfrac{B_3 T}{V^3}$

$\qquad + \dfrac{B_4 T}{V^4} + \dfrac{B_5 T}{V^5} + [\dfrac{C_1 (2 + 5.475 T_R)}{V}$

$\qquad + \dfrac{C_2 (3 + 5.475 T_R)}{2V^2} + \dfrac{C_3 (4 + 5.475 T_R)}{3V^3}$

$\qquad + \dfrac{C_4 (5 + 5.475 T_R)}{4V^4}$

$\qquad + \dfrac{C_5 (6 + 5.475 T_R)}{5V^5}] \, e^{-5.475T_R}$

$\qquad H_o \; = \;$ ideal gas enthalpy

5) $\quad (S - S_o^*)_T = -\dfrac{B_1}{V} - \dfrac{B_2}{2V^2} - \dfrac{B_3}{3V^3} - \dfrac{B_4}{4V^4}$

$$- \dfrac{B_5}{5V^5} + [\dfrac{C_1}{V} + \dfrac{C_2}{2V^2} + \dfrac{C_3}{3V^3}$$

$$+ \dfrac{C_4}{4V^4} + \dfrac{C_5}{5V^5}](\dfrac{5.475}{T_c}) \, e^{-5.475T_R}$$

$$+ R \ln (\dfrac{V}{V^*})$$

$S_o^* =$ reference state entropy, usually ideal

gas at one atmosphere pressure.

6) $\quad \ln (\dfrac{f}{P}) = -\ln (\dfrac{PV}{RT}) + \dfrac{1}{RT} [\dfrac{2A_1}{V} + \dfrac{3}{2}\dfrac{A_2}{V^2}$

$$+ \dfrac{4}{3}\dfrac{A_3}{V^3} + \dfrac{5}{4}\dfrac{A_4}{V^4} + \dfrac{6}{5}\dfrac{A_5}{V^5} + 2\dfrac{B_1 T}{V}$$

$$+ \dfrac{3}{2}\dfrac{B_2 T}{V^2} + \dfrac{4}{3}\dfrac{B_3 T}{V^3} + \dfrac{5}{4}\dfrac{B_4 T}{V^4} + \dfrac{6}{5}\dfrac{B_5 T}{V^5}$$

$$+ (\dfrac{2C_1}{V} + \dfrac{3}{2}\dfrac{C_2}{V^2} + \dfrac{4}{3}\dfrac{C_3}{V^3} + \dfrac{5}{4}\dfrac{C_4}{V^4}$$

$$+ \dfrac{6}{5}\dfrac{C_5}{V^5}) \, e^{-5.475T_R}]$$

Standard State $\quad \dfrac{f}{P} = 1.0$ for ideal gas.

$$f_o = P_{ideal} = \dfrac{RT}{V}$$

A   P   P   E   N   D   I   X   B

P-V-T DATA FITTING BY LINEAR PROGRAMMING

Part I Program

Approximating Function:

$$P = \frac{RT}{V} + \frac{A_1}{V^2} + \frac{A_2}{V^3} + \frac{A_3}{V^4} + \frac{A_4}{V^5} + \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V^2} + \frac{B_2 T}{V^3} + \frac{B_3 T}{V^4} + \frac{B_4 T}{V^5} + \frac{B_5 T}{V^6}$$

$$+ [\frac{C_1}{V^2} + \frac{C_2}{V^3} + \frac{C_3}{V^4} + \frac{C_4}{V^5} + \frac{C_5}{V^6}] \, e^{-5.475 T_R}$$

Fitting Criterion:

Minimize the maximum percentage deviation in pressure.

Input Information:

M - Number of data points

N - Number of equation coefficients

TC - Critical temperature

P - Pressure

T - Temperature

V - Volume

R - Gas Constant

Output Information:

Objective value - maximum percentage deviation in
pressure.

Basic Variables - indexes of the controlling data
points. Controlling data points
being those where the maximum

deviations occur,of which there will be N+1.

For indexes greater than M, attach a minus sign and add M. These indexes and their signs are required for Part II program. Data points with indexes greater than M are points at which P-equation is greater than P-experimental.

Part II Program

This program is basically a Gaussian-Elimination solution of a set of linear equations. The linear equations to be solved are the approximating function equations at the controlling data points.

Input Information:

N	-	number of coefficients plus one
R	-	gas constant
TC	-	critical temperature
**P	-	pressure
**T	-	temperature
**V	-	volume
**SG	-	sign of the index (+1.0 or -1.0)

** These values are for the controlling data points given by the Part I program.

Input Information for Checking:

      MM - total number of data points.

               (same as M for Part I)

   P,T,V - set of data used in the Part I program.

Output Information:

     1. The first value in the output solution is the maximum pressure deviation. This value should check with that obtained from the Part I program, if the solution for the equation coefficients is accurate.

     2. The remaining values in the solution list are the equation coefficients in the order which they appear in the equation.

     3. A check of the equation fit is printed out. This listing provides a further check on the solution for the equation coefficients. The maximum deviations should occur at the controlling data points if the equation fit is correct.

P-V-T FITTING PROGRAM - PART I

```
 $IBFTC MAIN     NODECK,NOLIST
**         COMMON A(22,550),B(22),C(550),F(550),K(22),RX(22),
**      1 M,MM,N,NA,BB
**         READ(5,1) M,N
** 1       FORMAT(2X,2I4)
**         READ(5,300) TC
**300       FORMAT(1H ,F15.8)
**         R=10.73147
**       NA=N+1
**       MM=M+M
**         DO 102 I=1,M
**         READ(5,101) P,T,V,
**101       FORMAT(1H ,3F15.8)
**         WRITE(6,400) I,P,T,V
**400       FORMAT(1H ,I3,3F15.8)
**         AT=1.0/(V*V)
**         AU=AT/V
**         AV=AU/V
**         AW=AV/V
**         AX=AW/V
**         EA=EXP(-5.475*T/TC)
**         F(I)=(P-R*T/V)/P
**         A(2,I)=AT/P
**         A(3,I)=AU/P
**         A(4,I)=AV/P
**         A(5,I)=AW/P
**         A(6,I)=AX/P
**         A(7,I)=AT*T/P
**         A(8,I)=AU*T/P
**         A(9,I)=AV*T/P
**         A(10,I)=AW*T/P
**         A(11,I)=AX*T/P
**         A(12,I)=AT*EA/P
**         A(13,I)=AU*EA/P
**         A(14,I)=AV*EA/P
**         A(15,I)=AW*EA/P
**102       A(16,I)=AX*EA/P
**         DO 5 J=1,M
**       JM=J+M
**       F(JM)=-F(J)
**         A(1,J)=0.01
**         A(1,JM)=0.01
          DO 5 I=2,NA
   5       A(I,JM)=-A(I,J)
          BB=0.00
          K(1)=1
          B(1)=1
          DO 7 I=2,NA
          XX=A(I,1)
          B(I)=-XX
          A(I,1)=0.00
```

```
        DO 7 J=2,MM
7       A(I,J)=A(I,J)-XX*A(1,J)
        DO 8 I=2,NA
        IF (B(I).GE.0.0) GO TO 8
        B(I)=-B(I)
        DO 9 J=1,MM
9       A(I,J)=-A(I,J)
8       CONTINUE
        DO 10 L=2,NA
        XX=A(L,1)
        JA=1
        DO 11 J=2,MM
        IF (A(L,J).LE.XX) GO TO 11
        XX=A(L,J)
        JA=J
11      CONTINUE
        K(L)=JA
        B(L)=B(L)/XX
        DO 12 J=1,MM
12      A(L,J)=A(L,J)/XX
        DO 13 I=1,NA
        IF (I.EQ.L) GO TO 13
        YY=A(I,JA)
        B(I)=B(I)-B(L)*YY
        DO 14 J=1,MM
14      A(I,J)=A(I,J)-A(L,J)*YY
13      CONTINUE
10      CONTINUE
40      DO 30 I=1,NA
        IF(B(I).GE.0.0) GO TO 30
        IA=I
        GO TO 50
30      CONTINUE
        GO TO 31
50      B(IA)=-B(IA)
        DO 51 J=1,MM
51      A(IA,J)=-A(IA,J)
        XX=0.00
        JA=0
        DO 52 J=1,MM
        DO 53 I=1,NA
        IF (J.EQ.K(I)) GO TO 52
53      CONTINUE
        IF (A(IA,J).LE.XX) GO TO 52
        XX=A(IA,J)
        JA=J
52      CONTINUE
        K(IA)=JA
        B(IA)=B(IA)/XX
        DO 54 J=1,MM
54      A(IA,J)=A(IA,J)/XX
        DO 55 I=1,NA
        IF (I.EQ.IA) GO TO 55
```

```
      YY=A(I,JA)
      B(I)=B(I)-B(IA)*YY
      DO 56 J=1,MM
56    A(I,J)=A(I,J)-A(IA,J)*YY
55    CONTINUE
      GO TO 40
31    DO 20 I=1,NA
      IA=K(I)
20    BB=BB+F(IA)*B(I)
      DO 21 J=1,MM
      C(J)=0.00
      DO 22 I=1,NA
      IA=K(I)
22    C(J)=C(J)+F(IA)*A(I,J)
21    C(J)=C(J)-F(J)
      WRITE (6,25)
25    FORMAT (1HO, 15X, 22H FOR INITIAL TABLEAU - )
      WRITE (6,26) BB
26    FORMAT (1HO, 16X, 21HOBJECTIVE FUNCTION = , E15.8)
      WRITE (6,27) (K(L), B(L), L=1,NA)
27    FORMAT (1H , 18X, 16HINDEP. VECTOR = , 14, 5X, E15.6)
      CALL SIMPLEX
67    CONTINUE
      STOP
      END
```

```
$IBFTC    DUAL      NODECK,NOLIST
          SUBROUTINE SIMPEX
          COMMON A(22,550),B(22),C(550),F(550),K(22),RX(22),
       1 M,MM,N,NA,BB
  399     QX=C(1)
          JA=1
          DO 300 J=2,MM
          IF (C(J).GE.QX) GO TO 300
          JA=J
          QX=C(J)
  300     CONTINUE
          IF (QX.GE.0.0) GO TO 330
          DO 301 I=1,NA
          IF (A(I,JA).LE.0.0) GO TO 302
          RX(I)=B(I)/A(I,JA)
          GO TO 301
  302     RX(I)=-1.00
  301     CONTINUE
          DO 303 I=1,NA
          IF (RX(I).LT.0.0) GO TO 303
          QA=RX(I)
          II=I
          GO TO 304
  303     CONTINUE
          WRITE (6,307)
  307     FORMAT (1HO, 15X, 20H UNBOUNDED SOLUTION.)
          GO TO 398
  304     IF (II.GE.NA) GO TO 310
          IC=II+1
          DO 305 I=IC,NA
          IF (RX(I).LT.0.0.OR.RX(I).GT.QA) GO TO 305
          IF (RX(I).EQ.QA) GO TO 306
          QA=RX(I)
          II=I
          GO TO 305
  306     IF (K(II).GE.K(I)) GO TO 305
          QA=RX(I)
          II=I
  305     CONTINUE
  310     DX=A(II,JA)
          B(II)=B(II)/DX
          DO 311 J=1,MM
  311     A(II,J)=A(II,J)/DX
          DO 312 I=1,NA
          IF (I.EQ.II) GO TO 312
          DXX=A(I,JA)
          B(I)=B(I)-DXX*B(II)
          DO 313 J=1,MM
          IF (J.EQ.JA) GO TO 314
          A(I,J)=A(I,J)-DXX*A(II,J)
          GO TO 313
```

```
314        A(I,J)=0.00
313        CONTINUE
312        CONTINUE
           BB=BB-C(JA)*B(II)
           DO 315 J=1,MM
           IF (J.EQ.JA) GO TO 315
           C(J)=C(J)-C(JA)*A(II,J)
315        CONTINUE
           C(JA)=0.00
           K(II)=JA
           GO TO 399
330        WRITE (6,331)
331        FORMAT (1HO, 30H THIS IS THE OPTIMUM SOLUTION. )
           WRITE (6,321) BB
321        FORMAT (1H , 20X, 22H OBJECTIVE FUNCTION = , E15.8)
           WRITE (6,322)
322        FORMAT (1HO, 25X, 48HBASIC VARIABLES   AND    VALUES
          1ARE AS FOLLOWS)
           WRITE (6,323) (K(I), B(I), I=1,NA)
323        FORMAT (1H , 29X, I4, 12X, E15.8)
398        CONTINUE
           RETURN
           END
```

P-V-T FITTING PROGRAM - PART I

SAMPLE OUTPUT

Index	P (psia)	T (°R)	V(ft^3/mole)

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE

Index	P (psia)	T (°R)	V(ft^3/mole)
1	99.15390848	401.68798720	39.06036032−
2	120.85990144	410.68799488	32.29404288
3	145.90188544	419.68798720	26.90453504
4	174.58847744	428.68799488	22.56472992
5	207.25768448	437.68798720	19.03493760
6	244.21812224	446.68799488	16.13327472
7	285.82249728	455.68798720	13.72297680
8	332.37942784	464.68799488	11.70887280
9	384.25630208	473.68798720	10.00636672
10	441.83523840	482.68799488	8.55905992
11	505.49830144	491.68798720	7.31971984+
12	575.67170560	500.68799488	6.14622424
13	652.86979584	509.68798720	5.19888340
14	737.62162688	518.68799488	4.38689720
15	830.69138944	527.68799232	3.63574996
16	933.00494336	536.68799488	2.91308352
17	1070.60359168	547.55998720	1.50666524−
18	7.34799992	401.68798720	582.54621696
19	14.69599984	401.68798720	289.17934336
20	29.39199968	401.68798720	142.50295552
21	44.08799872	401.68798720	93.56382720
22	58.78399936	401.68798720	69.05901504
23	73.47999936	401.68798720	54.34625856
24	88.17599744	401.68798720	44.50485504
25	7.34799992	437.68798720	635.96191232
26	14.69599984	437.68798720	316.35599872
27	29.39199968	437.68798720	156.55303936
28	44.08799872	437.68798720	103.22193792
29	58.78399936	437.68798720	76.58811264
30	73.47999936	437.68798720	60.59230656
31	88.17599744	437.68798720	49.89788864
32	117.56799872	437.68798720	36.48227872
33	146.95999872	437.68798720	28.48085184
34	176.35199488	437.68798720	23.08781888
35	7.34799992	473.68798720	689.08856320
36	14.69599984	473.68798720	343.20836608
37	29.39199968	473.68798720	170.25768832
38	44.08799872	473.68798720	112.57691264
39	58.78399936	473.68798720	83.75062464
40	73.47999936	473.68798720	66.44357184
41	88.17599744	473.68798720	54.88908672
42	117.56799872	473.68798720	40.40897120

Index	P (psia)	T (°R)	V(ft^3/mole)
43	146.95999872	473.68798720	31.76601952
44	176.35199488	473.68798720	25.93590400
45	220.43999488	473.68798720	20.12693872
46	293.91999744	473.68798720	14.26157520
47	367.39999744	473.68798720	10.61687192
48	7.34799992	509.68798720	742.09538048
49	14.69599984	509.68798720	369.93382912
50	29.39199968	509.68798720	183.82838784
51	44.08799872	509.68798720	121.78384000
52	58.78399936	509.68798720	90.76509184
53	73.47999936	509.68798720	72.14679232
54	88.17599744	509.68798720	59.72519296
55	117.56799872	509.68798720	44.18761856
56	146.95999872	509.68798720	34.88199360
57	176.35199488	509.68798720	28.63594528
58	220.43999488	509.68798720	22.39694688
59	293.91999744	509.68798720	16.12974992
60	367.39999744	509.68798720	12.32995280
61	440.87998976	509.68798720	9.76385640
62	587.83999488	509.68798720	6.41383152
63	7.34799992	545.68799232	795.01758464
64	14.69599984	545.68799232	396.56061440
65	29.39199968	545.68799232	197.31449344
66	44.08799872	545.68799232	130.89912320
67	58.78399936	545.68799232	97.69496064
68	73.47999936	545.68799232	77.76541568
69	88.17599744	545.68799232	64.46965120
70	117.56799872	545.68799232	47.85347072
71	146.95999872	545.68799232	37.88517280
72	176.35199488	545.68799232	31.21614144
73	220.43999488	545.68799232	24.55416032
74	293.91999744	545.68799232	17.87807936
75	367.39999744	545.68799232	13.84564192
76	440.87998976	545.68799232	11.13855072
77	587.83999488	545.68799232	7.70533936
78	734.79999488	545.68799232	5.57632512
79	881.75997952	545.68799232	3.99154912
80	7.34799992	563.68799232	821.44697344
81	14.69599984	563.68799232	409.84227328
82	29.39199968	563.68799232	204.03287296
83	44.08799872	563.68799232	135.42504064
84	58.78399936	563.68799232	101.12817280
85	73.47999936	563.68799232	80.54300288
86	88.17599744	563.68799232	66.81015744
87	117.56799872	563.68799232	49.65114816
88	146.95999872	563.68799232	39.35151328
89	176.35199488	563.68799232	32.47099104
90	220.43999488	563.68799232	25.59751776

Index	P (psia)	T (°R)	V(ft^3/mole)
91	293.91999744	563.68799232	18.70994560
92	367.39999744	563.68799232	14.55766320
93	440.87998976	563.68799232	11.77302528
94	587.83999488	563.68799232	8.26226696
95	734.79999488	563.68799232	6.11280864
96	881.75997952	563.68799232	4.60910420
97	1175.67998976	563.68799232	2.42510226-
98	1469.59998976	563.68799232	1.09623080
99	2204.39998464	563.68799232	0.90024870
100	2939.19997952	563.68799232	0.83891618
101	4408.79996928	563.68799232	0.76982896
102	5878.39995904	563.68799232	0.73528535+
103	7347.99986688	563.68799232	0.70849642
104	8817.59993856	563.68799232	0.68699481
105	11756.79991808	563.68799232	0.65964191
106	14695.99973376	563.68799232	0.63792878
107	17635.19987712	563.68799232	0.62122096
108	22043.99927296	563.68799232	0.60112927
109	29391.99946752	563.68799232	0.57617328-
110	14.69599984	581.68799232	423.10984704
111	73.47999936	581.68799232	83.29944192
112	146.95999872	581.68799232	40.79670560
113	293.91999744	581.68799232	19.51361344
114	440.87998976	581.69899232	12.37930080
115	587.83999488	581.68799232	8.78394576
116	734.79999488	581.68799232	6.58654952
117	881.75997952	581.68799232	5.10681412
118	1175.67998976	581.68799232	3.12513900
119	1469.59998976	581.68799232	1.74550962
120	2204.39998464	581.68799232	1.00669941+
121	2939.19997952	581.68799232	0.89954373+
122	4408.79996928	581.68799232	0.80507755
123	5878.39995904	581.68799232	0.76207427
124	7347.99986688	581.68799232	0.72964558
125	8817.59993856	581.68799232	0.70454858-
126	11756.79991808	581.68799232	0.67395283
127	14695.99973376	581.68799232	0.65026579
128	17635.19987712	581.68799232	0.63186603
129	22043.99927296	581.68799232	0.61001191
130	29391.99946752	581.68799232	0.58315250
131	14.69599984	617.68799232	449.60971776
132	73.47999936	617.68799232	88.77002112
133	146.95999872	617.68799232	43.65184064
134	293.91999744	617.68799232	21.06455104
135	440.87998976	617.68799232	13.52840480
136	587.83999488	617.68799232	9.74975704
137	734.79999488	617.68799232	7.45154968
138	881.75997952	617.68799232	5.92528616
139	1175.67998976	617.68799232	3.97533476
140	1469.59998976	617.68799232	2.78040788

Index	P (psia)	T (°R)	V(ft^3/mole)
141	2204.39998464	617.68799232	1.38033436
142	2939.19997952	617.68799232	1.06309713
143	4408.79996928	617.68799232	0.89037910
144	5878.39995904	617.68799232	0.82058691
145	7347.99986688	617.68799232	0.77617371
146	8817.59993856	617.68799232	0.74444998
147	11756.79991808	617.68799232	0.70342063
148	14695.99973376	617.68799232	0.67550376
149	17635.19987712	617.68799232	0.65350866
150	22043.99927296	617.68799232	0.62812968+
151	29391.99946752	617.68799232	0.59746341+
152	36739.99933440	617.68799232	0.57469284
153	14.69599984	653.68799232	476.06731264
154	73.47999936	653.68799232	94.20535168
155	146.95999872	653.68799232	46.47172672
156	293.91999744	653.68799232	22.58024000
157	440.87998976	653.68799232	14.62111040
158	587.83999488	653.68799232	10.63802120
159	734.79999488	653.68799232	8.23406800
160	881.75997952	653.68799232	6.62955272
161	1175.67998976	653.68799232	4.61333404
162	1469.59998976	653.68799232	3.41065248
163	2204.39998464	653.68799232	1.85901004
164	2939.19997952	653.68799232	1.29785269
165	4408.79996928	653.68799232	0.99682983
166	5878.39995904	653.68799232	0.88755922
167	7347.99986688	653.68799232	0.82834161
168	8817.59993856	653.68799232	0.78815823
169	11756.79991808	653.68799232	0.73528535
170	14695.99973376	653.68799232	0.70158772
171	17635.19987712	653.68799232	0.67550376
172	22043.99927296	653.68799232	0.64659993
173	29391.99946752	653.68799232	0.60860197-
174	36739.99933440	653.68799232	0.58745282
175	14.69599984	689.68799232	502.50374144
176	73.47999936	689.68799232	99.61248384
177	146.95999872	689.68799232	49.25636480
178	293.91999744	689.68799232	24.06772992
179	440.87998976	689.68799232	15.67151808
180	587.83999488	689.68799232	11.47693728
181	734.79999488	689.68799232	8.95313904
182	881.75997952	689.68799232	7.27530680
183	1175.67998976	689.68799232	5.16814660
184	1469.59998976	689.68799232	3.92105188
185	2204.39998464	689.68799232	2.27987810
186	2939.19997952	689.68799232	1.58477610
187	4408.79996928	689.68799232	1.12231475
188	5878.39995904	689.68799232	0.96510609
189	7347.99986688	689.68799232	0.88614927
190	8817.59993856	689.68799232	0.83398137

Index	P (psia)	T (°R)	V(ft^3/mole)
191	11756.79991808	689.68799232	0.76982896
192	14695.99973376	689.68799232	0.72823564
193	17635.19987712	689.68799232	0.69813335
194	22043.99927296	689.68799232	0.66542268
195	29391.99946752	689.68799232	0.62714272
196	36739.99933440	689.68799232	0.60042430
197	44087.99854592	689.68799232	0.58026211+
198	14.69599984	725.68799232	528.93312512
199	73.47999936	725.68799232	105.01256448
200	146.95999872	725.68799232	52.02690304
201	293.91999744	725.68799232	25.52702112
202	440.87998976	725.68799232	16.70077680
203	587.83999488	725.68799232	12.28765472
204	734.79999488	725.68799232	9.63696152
205	881.75997952	725.68799232	7.88863200
206	1175.67998976	725.68799232	5.67502112
207	1469.59998976	725.68799232	4.36306904
208	2204.39998464	725.68799232	2.64505338
209	2939.19997952	725.68799232	1.86958462
210	4408.79996928	725.68799232	1.26401405
211	5878.39995904	725.68799232	1.05393250
212	7347.99986688	725.68799232	0.94959671
213	8817.59993856	725.68799232	0.88473933
214	11756.79991808	725.68799232	0.80578251
215	14695.99973376	725.68799232	0.75643450
216	17635.19987712	725.68799232	0.72189089
217	22043.99927296	725.68799232	0.68452741
218	29391.99946752	725.68799232	0.64244061
219	36739.99933440	725.68799232	0.61339577
220	44087.99854592	725.68799232	0.59133016
221	14.69599984	761.68799232	555.34841856
222	73.47999936	761.68799232	110.40559872
223	146.95999872	761.68799232	54.79039104
224	293.91999744	761.68799232	26.97926208
225	440.87998976	761.68799232	17.70888608
226	587.83999488	761.68799232	13.07722272
227	734.79999488	761.68799232	10.29963480
228	881.75997952	761.68799232	8.45965896
229	1175.67998976	761.68799232	6.14876216
230	1469.59998976	761.68799232	4.76772284
231	2204.39998464	761.68799232	2.97004524
232	2939.19997952	761.68799232	2.12266942+
233	4408.79996928	761.68799232	1.41628788
234	5878.39995904	761.68799232	1.15474343
235	7347.99986688	761.68799232	1.01868394
236	8817.59993856	761.68799232	0.93620225-
237	11756.79991808	761.68799232	0.84385097
238	14695.99973376	761.68799232	0.78463336
239	17635.19987712	761.68799232	0.74585992
240	29391.99946752	761.68799232	0.65802047+
241	36739.99933440	761.68799232	0.62643775
242	44087.99854592	761.68799232	0.60246871

FOR INITIAL TABLEAU -

OBJECTIVE FUNCTION = -0.40152110E-02

INDEP. VECTOR =	1	0.987242E 00
INDEP. VECTOR =	98	0.289734E-01
INDEP. VECTOR =	343	0.122462E-01
INDEP. VECTOR =	14	0.106308E 00
INDEP. VECTOR =	109	0.615342E-02
INDEP. VECTOR =	259	0.316666E-01
INDEP. VECTOR =	477	0.664858E-02
INDEP. VECTOR =	232	0.220156E-01
INDEP. VECTOR =	484	0.343212E-02
INDEP. VECTOR =	471	0.404424E-01
INDEP. VECTOR =	239	0.771331E-02
INDEP. VECTOR =	384	0.130618E-01
INDEP. VECTOR =	145	0.274734E-02
INDEP. VECTOR =	245	0.980893E 00
INDEP. VECTOR =	394	0.332443E-04
INDEP. VECTOR =	382	0.134606E-01

THIS IS THE OPTIMUM SOLUTION

OBJECTIVE FUNCTION = 0.15957026E 01

BASIC VARIABLES AND VALUES ARE AS FOLLOWS

259 (-17)	0.11389451E 00
415 (-173)	0.36296422E 02
232	0.13209053E 00
367 (-125)	0.95700353E 01
339 (-97)	0.23864708E 00
351 (-109)	0.22129839E 01
102	0.21339985E 01
240	0.28167650E 01
243 (-1)	0.43130310E 00
150	0.33762138E 02
11	0.51209398E 00
151	0.65132731E 00
120	0.10159683E 00
197	0.99317753E 01
478 (-236)	0.38013893E 00
121	0.71483271E 00

P-V-T FITTING PROGRAM - PART II

```
     $IBFTC  CLARE      NODECK
**           DOUBLE PRECISION G(16,17),S,D,B,SIG,DIV(16),Y(16),Q,AST
**           DIMENSION X(16)
        4    FORMAT    (1H ,8HSINGULAR)
        5    FORMAT    (1H ,5HERROR)
**           N=16
**           R=10.73147
**           READ(5,550) TC
**      550  FORMAT(1H ,F15.8)
**           DO 52 I=1,N
**           READ(5,53) P,T,V,SG
**       53  FORMAT(1H ,3F15.8,F4.1)
**           AT=1.0/(V*V)
**           AU=AT/V
**           AV=AU/V
**           AW=AV/V
**           AX=AW/V
**           EA=EXP(-5.475*T/TC)
**           G(I,1)=0.01
**           G(I,2)=SG*AT/P
**           G(I,3)=SG*AU/P
**           G(I,4)=SG*AV/P
**           G(I,5)=SG*AW/P
**           G(I,6)=SG*AX/P
**           G(I,7)=SG*AT*T/P
**           G(I,8)=SG*AU*T/P
**           G(I,9)=SG*AV*T/P
**           G(I,10)=SG*AW*T/P
**           G(I,11)=SG*AX*T/P
**           G(I,12)=SG*AT*EA/P
**           G(I,13)=SG*AU*EA/P
**           G(I,14)=SG*AV*EA/P
**           G(I,15)=SG*AW*EA/P
**           G(I,16)=SG*AX*EA/P
**       52  G(I,17)=SG*(P-R*T/V)/P
             NN=N+1
             DO 70 J=1,N
        70   DIV(J)=ABS(G(1,J))
             DO 71 J=1,N
             DO 71 I=1,N
        71   G(I,J)=G(I,J)/DIV(J)
             K=N
        60   MAX=1
             Q=ABS(G(1,K))
             DO 65 I=2,K
             IF(ABS(G(I,K)).LT.Q) GO TO 65
             MAX=I
             Q=ABS(G(MAX,K))
        65   CONTINUE
```

```
          DO 62 J=1,NN
          AST=G(MAX,J)
          G(MAX,J)=G(K,J)
   62     G(K,J)=AST
          K=K-1
          IF(K.GE.2) GO TO 60
    9     K=N
   11     IF(G(K,K).NE.0.0) GO TO 14
   16     M=K-1
   22     IF(G(M,K).EQ.0.0) GO TO 20
   18     DO 19 J=1,K
          S=G(M,J)
          G(M,J)=G(K,J)
   19     G(K,J)=S
          S=G(M,NN)
          G(M,NN)=G(K,NN)
          G(K,NN)=S
          GO TO 14
   20     M=M-1
          IF(M.LT.0) GO TO 99
          IF(M.GT.0) GO TO 22
   23     WRITE(6,4)
          GO TO 401
   14     D=G(K,K)
          DO 26 J=1,K
   26     G(K,J)=G(K,J)/D
          G(K,NN)=G(K,NN)/D
          I=K-1
   30     IF(G(I,K).EQ.0.0) GO TO 28
   27     B=G(I,K)
          DO 29 J=1,K
   29     G(I,J)=G(I,J)-B*G(K,J)
          G(I,NN)=G(I,NN)-B*G(K,NN)
   28     I=I-1
          IF(I.LT.0) GO TO 99
          IF(I.GT.0) GO TO 30
   32     K=K-1
          IF(K.LT.1) GO TO 99
          IF(I.GT.1) GO TO 11
   34     IF(G(1,1).NE.0.0) GO TO 36
   35     WRITE(6,4)
          GO TO 401
   36     G(1,NN)=G(1,NN)/G(1,1)
          DO 40 I=2,N
          SIG=0.0
          NI=I-1
          DO 38 J=1,NI
   38     SIG=SIG+G(I,J)*G(J,NN)
   40     G(I,NN)=G(I,NN)-SIG
          DO 400 I=1,N
  400     Y(I)=G(I,NN)
```

```
        DO 63 I=1,N
   63   X(I)=Y(I)/DIV(I)
        WRITE (6,55)
   55   FORMAT (1HO,10X, 16HFINAL SOLUTIONS. )
        WRITE(6,56) (X(I),I=1,N)
   56   FORMAT(1H ,E15.8)
****C   CHECK OF SOLUTIONS.
        READ(5,57) MM
   57   FORMAT(1H ,I3)
        AM=MM
        SR=0.0
        SP=0.0
        WRITE(6,213)
  213   FORMAT(1H ,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),
      1 9X,6HP.EXP.,8X,7HP.CALC.,7X,8IIABS.DEV.,7X,8HPER.DEV.)
        DO 58 J=1,MM
        READ(5,59) P,T,V
   59   FORMAT(1H ,3F15.8)
        AT=1.0/(V*V)
        AU=AT/V
        AV=AU/V
        AW=AV/V
        AX=AW/V
        EA=EXP(-5.475*T/TC)
        PK=R*T/V+X(2)*AT+X(3)*AU+X(4)*AV+X(5)*AW+X(6)*AX+X(7)*
      1 AT*T+X(8)*AU*T+X(9)*AV*T+X(10)*AW*T+X(11)*AX*T+X(12)*
      2 AT*EA+X(13)*AU*EA+X(14)*AV*EA+X(15)*AW*EA+X(16)*AX*EA
        DEV=ABS(P-PK)
        PERC=DEV*100.0/P
        WRITE(6,61) V,T,P,PK,DEV,PERC
   61   FORMAT(1H ,F15.4,F15.2,4F15.4)
        SR=SR+DEV
   58   SP=SP+PERC
        SRA=SR/AM
        SPE=SP/AM
        WRITE(6,212) SRA,SPE
  212   FORMAT(1H ,9HAVE.DEV.=,F10.6,13HAVE.PER.DEV.=,F10.6)
        GO TO 401
   99   WRITE(6,5)
  401   CONTINUE
        STOP
        END
```

P-V-T FITTING PROGRAM - PART I

SAMPLE OUTPUT

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE

FINAL SOLUTIONS
```
 0.15957249E 01
-0.26280181E 05
 0.96207443E 05
-0.21501424E 06
 0.17530775E 06
-0.47329448E 05
 0.27269119E 02
-0.12725418E 03
 0.29627500E 03
-0.24136579E 03
 0.66861749E 02
 0.92167559E 05
-0.49328657E 07
 0.14323348E 08
-0.13172478E 08
 0.38213556E 07
```

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
39.0604	401.69	99.1539	100.7361	1.5822	1.5957-
32.2940	410.69	120.8599	122.4884	1.6285	1.3474
26.9045	419.69	145.9019	147.4381	1.5363	1.0529
22.5647	428.69	174.5885	175.8349	1.2464	0.7139
19.0349	437.69	207.2577	207.9322	0.6745	0.3254
16.1333	446.69	244.2181	244.0367	0.1815	0.0743
13.7230	455.69	285.8225	284.5093	1.3132	0.4594
11.7089	464.69	332.3794	329.6126	2.7668	0.8324
10.0064	473.69	384.2563	379.8604	4.3959	1.1440
8.5591	482.69	441.8352	435.6334	6.2018	1.4037
7.3197	491.69	505.4983	497.4319	8.0664	1.5957+
6.1462	500.59	575.6717	570.8441	4.8276	0.8386
5.1989	509.69	652.8698	648.5577	4.3121	0.6605
4.3869	518.69	737.6216	733.3795	4.2421	0.5751
3.6357	527.69	830.6914	829.5576	1.1338	0.1365
2.9131	536.69	933.0049	939.2325	6.2276	0.6675
1.5067	547.56	1070.6036	1087.6871	17.0835	1.5957-
582.5462	401.69	7.3480	7.3593	0.0113	0.1534
289.1793	401.69	14.6960	14.7415	0.0455	0.3094
142.5030	401.69	29.3920	29.5622	0.1702	0.5791
93.5638	401.69	44.0880	44.4599	0.3719	0.8435
69.0590	401.69	58.7840	58.4292	0.6452	1.0975
54.3463	401.69	73.4800	74.4377	0.9577	1.3033
44.5049	401.69	88.1760	89.5032	1.3272	1.5052
635.9619	437.69	7.3480	7.3530	0.0050	0.0685
316.3560	437.69	14.6960	14.7149	0.0189	0.1285
156.5530	437.69	29.3920	29.4594	0.0674	0.2292

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
103.2219	437.69	44.0880	44.2479	0.1599	0.3627
76.5881	437.69	58.7840	59.0354	0.2514	0.4276
60.5923	437.69	73.4800	73.8374	0.3574	0.4863
49.8979	437.69	88.1760	88.6788	0.5028	0.5702
36.4823	437.69	117.5680	118.4503	0.8823	0.7505
28.4809	437.69	146.9600	147.8713	0.9113	0.6201
23.0878	437.69	176.3520	177.2767	0.9247	0.5244
689.0886	473.69	7.3480	7.3505	0.0025	0.0338
343.2084	473.69	14.6960	14.7046	0.0086	0.0582
170.2577	473.69	29.3920	29.4224	0.0304	0.1033
112.5769	473.69	44.0880	44.1592	0.0712	0.1614
83.7506	473.69	58.7840	58.8951	0.1111	0.1890
66.4436	473.69	73.4800	73.6403	0.1603	0.2181
54.8891	473.69	88.1760	88.4057	0.2297	0.2605
40.4090	473.69	117.5680	118.0167	0.4487	0.3817
31.7660	473.69	146.9600	147.4031	0.4431	0.3015
25.9359	473.69	176.3520	177.0209	0.6689	0.3793
20.1269	473.69	220.4400	220.9677	0.5277	0.2394
14.2616	473.69	293.9200	293.3238	0.5962	0.2028
10.6169	473.69	367.4000	364.9076	2.4923	0.6784
742.0954	509.69	7.3480	7.3492	0.0012	0.0158
369.9338	509.69	14.6960	14.6993	0.0033	0.0224
183.8284	509.69	29.3920	29.4049	0.0129	0.0439
121.7838	509.69	44.0880	44.1172	0.0292	0.0661
90.7651	509.69	58.7840	58.8296	0.0456	0.0776
72.1468	509.69	73.4800	73.5471	0.0671	0.0913
59.7252	509.69	88.1760	88.2755	0.0995	0.1129
44.1876	509.69	117.5680	117.7507	0.1827	0.1554
34.8820	509.69	146.9600	147.1364	0.1764	0.1200
28.6359	509.69	176.3520	176.6802	0.3282	0.1861
22.3969	509.69	220.4400	220.8504	0.4104	0.1862
16.1298	509.69	293.9200	294.2850	0.3650	0.1242
12.3300	509.69	367.4000	367.4251	0.0251	0.0068
9.7639	509.69	440.8800	439.7815	1.0985	0.2492
6.4138	509.69	587.8400	581.4405	6.3995	1.0886
795.0176	545.69	7.3480	7.3485	0.0005	0.0070
396.5606	545.69	14.6960	14.6972	0.0012	0.0079
197.3145	545.69	29.3920	29.3967	0.0047	0.0161
130.8991	545.69	44.0880	44.0972	0.0092	0.0209
97.6950	545.69	58.7840	58.7951	0.0111	0.0188
77.7654	545.69	73.4800	73.4962	0.0162	0.0220
64.4697	545.69	88.1760	88.2076	0.0316	0.0359
47.8535	545.69	117.5680	117.6215	0.0535	0.0455
37.8852	545.69	146.9600	147.0135	0.0535	0.0364
31.2161	545.69	176.3520	176.4969	0.1449	0.0821
24.5542	545.69	220.4400	220.6448	0.2048	0.0929
17.8781	545.69	293.9200	294.1873	0.2673	0.0909
13.8456	545.69	367.4000	367.8763	0.4763	0.1296
11.1386	545.69	440.8800	441.5984	0.7184	0.1629
7.7053	545.69	587.8400	588.8692	1.0292	0.1751
5.5763	545.69	734.8000	735.0322	0.2322	0.0316

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
3.9915	545.69	881.7600	885.6750	3.9150	0.4440
821.4470	563.69	7.3480	7.3484	0.0004	0.0056
409.8423	563.69	14.6960	14.6969	0.0009	0.0064
204.0329	563.69	29.3920	29.3948	0.0028	0.0096
135.4250	563.69	44.0880	44.0941	0.0061	0.0139
101.1282	563.69	58.7840	58.7893	0.0053	0.0090
80.5430	563.69	73.4800	73.4875	0.0075	0.0102
66.8102	563.69	88.1760	88.1960	0.0200	0.0227
49.6511	563.69	117.5680	117.5990	0.0310	0.0264
39.3515	563.69	146.9600	147.0040	0.0440	0.0299
32.4710	563.69	176.3520	176.4645	0.1125	0.0638
25.5975	563.69	220.4400	220.5895	0.1495	0.0678
18.7099	563.69	293.9200	294.1637	0.2437	0.0829
14.5577	563.69	367.4000	367.8980	0.4980	0.1355
11.7730	563.69	440.8800	441.8307	0.9507	0.2156
8.2623	563.69	587.8400	589.8373	1.9973	0.3398
6.1128	563.69	734.8000	737.9580	3.1581	0.4298
4.6091	563.69	881.7600	888.2284	6.4684	0.7336
2.4251	563.69	1175.6800	1194.4406	18.7606	1.5957-
1.0962	563.69	1469.6000	1486.4647	16.8647	1.1476
0.9002	563.69	2204.4000	2207.6287	3.2287	0.1465
0.8389	563.69	2939.2000	2892.9321	46.2679	1.5742
0.7698	563.69	4408.8000	4435.6738	26.8738	0.6095
0.7353	563.69	5878.4000	5784.5967	93.8033	1.5957+
0.7085	563.69	7347.9998	7276.1425	71.8573	0.9779
0.6870	563.69	8817.5999	8874.1005	56.5006	0.6408
0.6596	563.69	11756.7999	11630.5234	126.2765	1.0741
0.6379	563.69	14695.9996	14617.1074	78.8923	0.5368
0.6212	563.69	17635.1998	17569.6738	65.5261	0.3716
0.6011	563.69	22043.9994	22122.2538	78.2544	0.3550
0.5762	563.69	29391.9992	29861.0312	469.0317	1.5958-
423.1098	581.69	14.6960	14.6970	0.0010	0.0066
83.2994	581.69	73.4800	73.4900	0.0100	0.0136
40.7967	581.69	146.9600	147.0273	0.0673	0.0458
19.5136	581.69	293.9200	294.2660	0.3460	0.1177
12.3793	581.69	440.8800	442.0022	1.1223	0.2545
8.7839	581.69	587.8400	590.1670	2.3270	0.3959
6.5865	581.69	734.8000	739.8288	5.0288	0.6844
5.1068	581.69	881.7600	888.5701	6.8102	0.7723
3.1251	581.69	1175.6800	1192.8554	17.1754	1.4609
1.7455	581.69	1469.6000	1491.6596	22.0596	1.5011
1.0067	581.69	2204.4000	2169.2267	35.1733	1.5956+
0.8995	581.69	2939.2000	2892.2976	46.9024	1.5958+
0.8051	581.69	4408.8000	4458.2197	49.4197	1.1209
0.7621	581.69	5878.4000	5822.3418	56.0582	0.9536
0.7296	581.69	7347.9998	7345.8867	2.1132	0.0288
0.7045	581.69	8817.5999	8958.3134	140.7135	1.5958-
0.6740	581.69	11756.7999	11661.3974	95.4025	0.8115
0.6503	581.69	14695.9996	14537.2460	158.7537	1.0803

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
0.6319	581.69	17635.1998	17420.3476	214.8523	1.2183
0.6100	581.69	22043.9994	21834.1816	209.8179	0.9518
0.5832	581.69	29391.9992	29291.1952	100.8042	0.3430
449.6097	617.69	14.6960	14.6976	0.0016	0.0107
88.7700	617.69	73.4800	73.5100	0.0300	0.0409
43.6518	617.69	146.9600	147.0899	0.1299	0.0884
21.0646	617.69	293.9200	294.6250	0.7050	0.2399
13.5284	617.69	440.8800	442.3709	1.4909	0.3382
9.7498	617.69	587.8400	590.3028	2.4628	0.4190
7.4515	617.69	734.8000	740.0801	5.2801	0.7186
5.9253	617.69	881.7600	888.8056	7.0456	0.7990
3.9753	617.69	1175.6800	1189.8388	14.1588	1.2043
2.7804	617.69	1469.6000	1489.9418	20.3418	1.3842
1.3803	617.69	2204.4000	2173.9406	30.4594	1.3818
1.0631	617.69	2939.2000	2892.6408	46.5592	1.5841
0.8904	617.69	4408.8000	4403.7583	5.0417	0.1144
0.8206	617.69	5878.4000	5865.3301	13.0699	0.2223
0.7762	617.69	7347.9998	7381.3676	33.3678	0.4541
0.7444	617.69	8817.5999	8920.0078	102.4078	1.1614
0.7034	617.69	11756.7999	11776.0625	19.2626	0.1638
0.6755	617.69	14695.9996	14541.8808	154.1189	1.0487
0.6535	617.69	17635.1998	17393.1640	242.0359	1.3725
0.6281	617.69	22043.9994	21692.2508	351.7485	1.5957+
0.5975	617.69	29391.9992	28922.9684	469.0308	1.5958+
0.5747	617.69	36739.9992	36352.9824	387.0171	1.0534
476.0673	653.69	14.6960	14.6987	0.0027	0.0185
94.2054	653.69	73.4800	73.5347	0.0547	0.0745
46.4717	653.69	146.9600	147.1580	0.1980	0.1348
22.5802	653.69	293.9200	294.8587	0.9387	0.3194
14.6211	653.69	440.8800	442.7273	1.8473	0.4190
10.6380	653.69	587.8400	590.7226	2.8827	0.4904
8.2341	653.69	734.8000	739.5775	4.7775	0.6502
6.6296	653.69	881.7600	888.5693	6.8094	0.7722
4.6133	653.69	1175.6800	1187.5926	11.9126	1.0133
3.4107	653.69	1469.6000	1483.0101	13.4101	0.9125
1.8590	653.69	2204.4000	2207.1749	2.7749	0.1259
1.2979	653.69	2939.2000	2922.9897	16.2103	0.5515
0.9968	653.69	4408.8000	4368.1831	40.6169	0.9213
0.8876	653.69	5878.4000	5884.7830	6.3830	0.1086
0.8283	653.69	7347.9998	7362.3947	14.3949	0.1959
0.7882	653.69	8817.5999	8847.2087	29.6088	0.3358
0.7353	653.69	11756.7999	11785.2075	28.4076	0.2416
0.7016	653.69	14695.9996	14570.3588	125.6409	0.8549
0.6755	653.69	17635.1998	17462.9252	172.2747	0.9769
0.6466	653.69	22043.9994	21732.2988	311.7007	1.4140
0.6086	653.69	29391.9992	29860.9968	468.9976	1.5957-
0.5875	653.69	36739.9992	36194.7420	545.2573	1.4841
502.5037	689.69	14.6960	14.6998	0.0038	0.0257

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
99.6125	689.69	73.4800	73.5614	0.0814	0.1108
49.2564	689.69	146.9600	147.2499	0.2899	0.1973
24.0677	689.69	293.9200	295.0407	1.1207	0.3813
15.6715	689.69	440.8800	443.1884	2.3084	0.5236
11.4769	689.69	587.8400	591.3456	3.5056	0.5964
8.9531	689.69	734.8000	739.9436	5.1436	0.7000
7.2753	689.69	881.7600	888.0238	6.2638	0.7104
5.1681	689.69	1175.6800	1185.0877	9.4077	0.8002
3.9211	689.69	1469.6000	1476.8746	7.2746	0.4950
2.2799	689.69	2204.4000	2205.0561	0.6561	0.0298
1.5848	689.69	2939.2000	2922.2157	16.9843	0.5779
1.1223	689.69	4408.8000	4388.0654	20.7346	0.4703
0.9651	689.69	5878.4000	5903.5646	25.1647	0.4281
0.8861	689.69	7347.9998	7363.2120	15.2122	0.2070
0.8340	689.69	8817.5999	8856.3151	38.7152	0.4391
0.7698	689.69	11756.7999	11727.7795	29.0204	0.2468
0.7282	689.69	14695.9996	14612.1960	83.8037	0.5702
0.6981	689.69	17635.1998	17500.5702	134.6296	0.7634
0.6654	689.69	22043.9994	21767.4702	276.5293	1.2544
0.6271	689.69	29391.9992	29007.3600	384.6392	1.3087
0.6004	689.69	36739.9992	36226.5076	513.4917	1.3976
0.5803	689.69	44087.9988	43384.4736	703.5254	1.5957+
528.9331	725.69	14.6960	14.7004	0.0044	0.0302
105.0126	725.69	73.4800	73.5774	0.0974	0.1325
52.0269	725.69	146.9600	147.3159	0.3559	0.2422
25.5270	725.69	293.9200	295.2605	1.3405	0.4561
16.7008	725.69	440.8800	443.4717	2.5917	0.5879
12.2877	725.69	587.8400	591.8361	3.9961	0.6798
9.6370	725.69	734.8000	740.4007	5.6007	0.7622
7.8886	725.69	881.7600	887.0359	5.2759	0.5983
5.6750	725.69	1175.6800	1183.1112	7.4312	0.6321
4.3631	725.69	1469.6000	1474.5426	4.9427	0.3363
2.6451	725.69	2204.4000	2193.2287	11.1713	0.5068
1.8696	725.69	2939.2000	2902.1612	37.0388	1.2602
1.2640	725.69	4408.8000	4401.5530	7.2470	0.1644
1.0539	725.69	5878.4000	5916.3138	37.9138	0.6450
0.9496	725.69	7347.9998	7395.0576	47.0578	0.6404
0.8847	725.69	8817.5999	8857.6470	40.0471	0.4542
0.8058	725.69	11756.7999	11728.6789	28.1210	0.2392
0.7564	725.69	14695.9996	14611.7118	84.2878	0.5735
0.7219	725.69	17635.1998	17473.7260	161.4739	0.9156
0.6845	725.69	22043.9994	21781.3154	262.6841	1.1916
0.6424	725.69	29391.9992	28999.7772	392.2222	1.3345
0.6134	725.69	36739.9992	36272.8332	467.1660	1.2715
0.5913	725.69	44087.9988	43671.7504	416.2485	0.9441
555.3484	761.69	14.6960	14.7010	0.0050	0.0341
110.4056	761.69	73.4800	73.5859	0.1059	0.1441
54.7904	761.69	146.9600	147.3499	0.3899	0.2653
26.9793	761.69	293.9200	295.3395	1.4195	0.4830

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
17.7089	761.69	440.8800	443.7584	2.8784	0.6529
13.0772	761.69	587.8400	592.2655	4.4255	0.7528
10.2996	761.69	734.8000	740.6798	5.8798	0.8002
8.4597	761.69	881.7600	887.8070	6.0470	0.6858
6.1488	761.69	1175.6800	1182.0811	6.4011	0.5445
4.7677	761.69	1469.6000	1473.6428	4.0428	0.2751
2.9700	761.69	2204.4000	2183.0381	21.3619	0.9691
2.1227	761.69	2939.2000	2892.2982	46.9017	1.5957+
1.4163	761.69	4408.8000	4382.2837	26.5163	0.6014
1.1547	761.69	5878.4000	5888.4962	10.0962	0.1718
1.0187	761.69	7347.9998	7431.2811	83.2813	1.1334
0.9362	761.69	8817.5999	8958.3100	140.7101	1.5958-
0.8439	761.69	11756.7999	11758.9757	2.1758	0.0185
0.7846	761.69	14695.9996	14707.7120	11.7123	0.0797
0.7459	761.69	17635.1998	17507.4580	127.7419	0.7244
0.6580	761.69	29391.9992	28922.9736	469.0259	1.5958+
0.6264	761.69	36739.9992	36243.4256	496.5737	1.3516
0.6025	761.69	44087.9988	43834.0560	253.9429	0.5760

AVE. DEV. = 50.261772

AVE.PER.DEV. = 0.566961

Example Problem

The Part I program is the actual linear programming portion of the procedure. Use of this program and the meaning of the output is best illustrated by a simple example. The statements in the program which need to be changed for a particular fitting problem are indicated in the program listing by **.

Data: $P_i - T_i$ $i = 1, 30$

Approximating Function:

$$P = a_o + a_1 T + a_2 T^2$$

Objective:

Minimize the maximum absolute deviation in P.

M = 30 (Number of data points)

N = 3 (Number of equation coefficients)

Statements in the program listing indicated by ** are replaced by the following.

```
        COMMON   A(4,60), B(4), C(60), F(60), K(4),
                 RX(4), M, MM, NN, NA, BB
        READ (5,1) M,N
1       FORMAT (2X, 2I4)
        NA = N + 1
        MM = M + M
        DO 102 I = 1, M
```

```
        READ (5,101) P,T
101     FORMAT (1H  , 2F15.8)
        WRITE (6,400) I, P, T
400     FORMAT (1H  , I3, 2F 15.8)
        F(I) = P
        A(2,I) = 1.0
        A(3,I) = T
102     A(4,I) = T**2
        DO 5 J = 1, M
        JM = J + M
        F(JM) = -F(J)
        A(1,J) = 1.0
        A(1,JM) = 1.0
```

For minimization of the maximum percentage deviation
in P, the following modifications are made:

```
        F(I) = 1.0
        A(2,I) = 1.0/P
        A(3,I) = T/P
102     A(4,I) = T**2/P
        A(1,J) = 0.01
        A(1,JM) = 0.01
```

Note: The COMMON statement for the subroutine must be made
      identical to that of the main program.

      The Part I program will give the following output:

1) Input data listing.

$$\underline{I} \qquad \underline{P} \qquad \underline{T} \qquad\qquad 1 < \underline{I} < 30$$

2)   A solution for the initial tableau. This is of no

   interest to the user.

3)   The optimum solution.

   OBJECTIVE FUNCTION = X.XXXX

   BASIC VARIABLES AND VALUES ARE AS FOLLOWS

2	X.XXXX
20	X.XXXX
7	X.XXXX
53	X.XXXX

   The objective function value is the maximum absolute
or percentage deviation of the fit, depending upon which
criterion was used.

   The basic variable indexes indicate the data points
at which the maximum deviation occurs. Some of the indexes
will be greater than the number of data points. For these
values attach a minus sign and add the number of data points.

   i.e.   53 ⟶ -53 + 30 = -23

   This index corresponds to data point number 23. The
sign of the index is required for Part II program.

Part II Program:

   This program uses the results of the Part I program
to solve for the equation coefficients. The program is simply
a Gaussian Elimination solution method for a set of linear
equations. The final portion of the program is a built in
check of the fitting procedure and need not be included.

Statements which must be changed for the particular fitting problem are indicated by **. The portion of the program following **** may be omitted entirely.

For the particular example problem the set of linear equations to be solved is:

$$
\begin{bmatrix}
1.0 & 1.0 & T_2 & (T_2)^2 \\
1.0 & 1.0 & T_{20} & (T_{20})^2 \\
1.0 & 1.0 & T_7 & (T_7)^2 \\
1.0 & -1.0 & -T_{23} & -(T_{23})^2
\end{bmatrix}
\begin{bmatrix}
\lambda \\
a_o \\
a_1 \\
a_2
\end{bmatrix}
=
\begin{bmatrix}
P_2 \\
P_{20} \\
P_7 \\
-P_{23}
\end{bmatrix}
$$

$$N = \text{number of coefficients} + 1 = 4$$

The subscripts refer to the indexes of the data point listing from the Part I program. The reason for obtaining the signs of the controlling data points is obvious in the above example.

The λ value to be solved for is the maximum deviation of the fit and should correspond to the value obtained from the Part I program.

If minimizing of the maximum percentage deviation was used in the Part I program, the set of equations to be solved would be,

$$
\begin{bmatrix}
0.01 & 1.0/P_2 & T_2/P_2 & (T_2)^2/P_2 \\
0.01 & 1.0/P_{20} & T_{20}/P_{20} & (T_{20})^2/P_{20} \\
0.01 & 1.0/P_7 & T_7/P_7 & (T_7)^2/P_7 \\
0.01 & -1.0/P_{23} & -T_{23}/P_{23} & -(T_{23})^2/P_{23}
\end{bmatrix}
\begin{bmatrix}
\lambda \\
a_o \\
a_1 \\
a_2
\end{bmatrix}
=
\begin{bmatrix}
1.0 \\
1.0 \\
1.0 \\
-1.0
\end{bmatrix}
$$

This is assuming that the same set of controlling data points were obtained from the linear program using this different fitting criterion.

A P P E N D I X   C

P-V-T FITTING FOR IMPROVED THERMODYNAMIC PROPERTIES

Part I Program

Approximating Function:

$$P = \frac{RT}{V} + \frac{A_1}{V^2} + \frac{A_2}{V^3} + \frac{A_3}{V^4} + \frac{A_4}{V^5} + \frac{A_5}{V^6}$$

$$+ \frac{B_1 T}{V^2} + \frac{B_2 T}{V^3} + \frac{B_3 T}{V^4} + \frac{B_4 T}{V^5} + \frac{B_5 T}{V^6}$$

$$+ \frac{C_1}{V^2} e^{-5.475T_R} + \frac{C_2}{V^3} e^{-5.475T_R} + \frac{C_3}{V^4} e^{-5.475T_R}$$

$$+ \frac{C_4}{V^5} e^{-5.475T_R} + \frac{C_5}{V^6} e^{-5.475T_R}$$

Derived Function:

$$(H-H_o)_T = J^* \left[2\frac{A_1}{V} + \frac{3}{2}\frac{A_2}{V^2} + \frac{4}{3}\frac{A_3}{V^3} + \frac{5}{4}\frac{A_4}{V^5} + \frac{6}{5}\frac{A_5}{V^6} \right.$$

$$+ \frac{B_1 T}{V} + \frac{B_2 T}{V^2} + \frac{B_3 T}{V^3} + \frac{B_4 T}{V^4} + \frac{B_5 T}{V^5}$$

$$+ \frac{C_1 (2 + 5.475T_R) e^{-5.475T_R}}{V}$$

$$+ \frac{C_2 (3 + 5.475T_R) e^{-5.475T_R}}{2V^2}$$

$$+ \frac{C_3 (4 + 5.475T_R) e^{-5.475T_R}}{3V^3}$$

$$+ \frac{C_4(5 + 5.475T_R)e^{-5.475T_R}}{4V^4}$$

$$+ \frac{C_5(6 + 5.475T_R)e^{-5.475T_R}}{5V^5} \Big]$$

J - units conversion factor.

The function in brackets has the units of PV.

Fitting Criterion:

Minimize the maximum percentage deviation in pressure subject to the absolute deviations in $(H-H_o)_T$ values being less than or equal to 2.0 BTU per pound.

Input Information:

M - Total number of data points of both types

M1 - Number of P-V-T data points

M2 - Number of $(H-H_o)_T$ data points

N - Number of equation coefficients

TC - Critical temperature

WT - Molecular weight

CONST - Specified maximum deviation in $(H-H_o)_T$

R - gas constant

CON - Conversion factor for $(H-H_o)_T$ in units of PV to BTU/lb.

P - pressure

T - temperature

V - volume

H - enthalpy departure $(H-H_o)_T$

Output Information:

1) Objective value - maximum percentage deviation of the
   P-V-T fit.

2) Indexes of the controlling data points.

   For indexes greater than M, attach a minus sign and add
   M to find the corresponding data point along with its
   sign. Separate the data points into P-V-T and $(H-H_o)_T$
   groups.

   Controlling data points are the ones where the maximum
deviations occur. Data points with indexes greater than M
correspond to

$$P_{calc.} > P_{exp.}$$
$$(H-H_o)_{Tcalc.} > (H-H_o)_{Texp.}$$

Part II Program

This program is basically a Gaussian Elimination
solution of a set of linear equations. The linear equations
to be solved are the approximating or derived functions at
the controlling data points.

Input Information:

   N - Number of equation coefficients plus one

   R - gas constant

   TC - critical temperature

   WT - molecular weight

CONST - specified maximum error in $(H-H_o)_T$

N1 - number of P-V-T controlling data points

N2 - N1 + 1

CON - conversion factor for $(H-H_o)_T$ from units of

         PV to BTU/lb

**P - pressure

**T - temperature

**V - volume

**SG - sign of the index

**   These values are for the controlling P-V-T data points given by the Part I program.

*H - enthalpy departure $(H-H_o)_T$

*T - temperature

*V - volume

*SG - sign of the index

*   These values are for the controlling $(H-H_o)_T$ data points given by the Part I program.

For the solution checking portion of the program:

M - total number of data points

M1 - number of P-V-T data points

Input the complete P-V-T and $(H-H_o)_T$ data deck from the Part I program.

Output:

1) The maximum percentage deviation in pressure. This value should equal that obtained from the Part I program.

2) The equation coefficients in the order which they appear in the equation.

3) A check of the calculated pressures and enthalpy departures. A further check of the validity of the solution is available by noting that the maximum errors in pressure and enthalpy departure occur at the controlling data points.

P-V-T AND ENTHALPY FITTING PROGRAM - PART I

```
      $IBFTC MAIN      NODECK,NOLIST
**           COMMON A(16,550),B(16),C(550),F(550),K(16),RX(16),
**         1 M,MM,N,NA,BB
**           READ(5,1) M,M1,M2,N
**     1     FORMAT(2X,4I4)
**           READ(5,300) TC,WT
**   300     FORMAT(1H ,2F15.8)
**           READ(5,2) CONST
**     2     FORMAT(1H ,F10.4)
**           R=10.73147
**           CON=144.0/(WT*778.173)
**         NA=N+1
**           M11=M1+1
**           MM=M+M
**           DO 102 I=1,M1
**           READ(5,101) P,T,V
**   101     FORMAT(1H ,3F15.8)
**           WRITE(6,400) I,P,T,V
**   400     FORMAT(1H ,I3,3F15.8)
**           AT=1.0/(V*V)
**           AU=AT/V
**           AV=AU/V
**           AW=AV/V
**           AX=AW/V
**           EA=EXP(-5.475*T/TC)
**           F(I)=(P-R*T/V)/P
**           A(2,I)=AT/P
**           A(3,I)=AU/P
**           A(4,I)=AV/P
**           A(5,I)=AW/P
**           A(6,I)=AX/P
**           A(7,I)=AT*T/P
**           A(8,I)=AU*T/P
**           A(9,I)=AV*T/P
**           A(10,I)=AW*T/P
**           A(11,I)=AX*T/P
**           A(12,I)=AT*EA/P
**           A(13,I)=AU*EA/P
**           A(14,I)=AV*EA/P
**           A(15,I)=AW*EA/P
**   102     A(16,I)=AX*EA/P
**           DO 401 I=M11,M
**           READ(5,101) H,T,V
**           WRITE(6,400) I,H,T,V
**           AT=CON/V
**           AU=AT/V
**           AV=AU/V
**           AW=AV/V
**           AX=AW/V
```

```
**            EB=5.475*T/TC
**            EC=EXP(-EB)
**            ET=(2.0+EB)*EC
**            EU=ET+EC
**            EV=EU+EC
**            EW=EV+EC
**            EX=EW+EC
**            F(I)=H
**            A(2,I)=2.0*AT
**            A(3,I)=1.5*AU
**            A(4,I)=4.0*AV/3.0
**            A(5,I)=1.25*AW
**            A(6,I)=6.0*AX/5.0
**            A(7,I)=T*AT
**            A(8,I)=T*AU
**            A(9,I)=T*AV
**            A(10,I)=T*AW
**            A(11,I)=T*AX
**            A(12,I)=ET*AT
**            A(13,I)=EU*AU/2.0
**            A(14,I)=EV*AV/3.0
**            A(15,I)=EW*AW/4.0
**    401     A(16,I)=EX*AX/5.0
              WRITE(6,3) M1,M2,CONST
      3       FORMAT (1H0, 5X, I4, 23H POINTS LESS THAN LAMBDA,/6X,
          1 I4, 17H POINTS    LESS THAN , E15.6)
              DO 5 J=1,M1
              JM=J+M
              F(JM)=-F(J)
              A(1,J)=0.01
              A(1,JM)=0.01
              DO 5 I=2,NA
      5       A(I,JM)=-A(I,J)
              DO 6J=M11,M
              JM=J+M
              F(JM)=-F(J)-CONST
              F(J)=F(J)-CONST
              A(1,J)=0.00
              A(1,JM)=0.00
              DO 6 I=2,NA
      6       A(I,JM)= -A(I,J)
              BB=0.00
              K(1)=1
              B(1)=1
              DO 7 I=2,NA
              XX=A(I,1)
              B(I)=-XX
              A(I,1)=0.00
              DO 7 J=2,MM
      7       A(I,J)=A(I,J)-XX*A(1,J)
              DO 8 I=2,NA
```

```
          IF (B(I).GE.0.0) GO TO 8
          B(I)=-B(I)
          DO 9 J=1,MM
   9      A(I,J)=-A(I,J)
   8      CONTINUE
          DO 10 L=2,NA
          XX=A(L,1)
          JA=1
          DO 11 J=2,MM
          IF (A(L,J).LE.XX) GO TO 11
          XX=A(L,J)
          JA=J
  11      CONTINUE
          K(L)=JA
          B(L)=B(L)/XX
          DO 12 J=1,MM
  12      A(L,J)=A(L,J)/XX
          DO 13 I=1,NA
          IF (I.EQ.L) GO TO 13
          YY=A(I,JA)
          B(I)=B(I)=B(L)*YY
          DO 14 J=1,MM
  14      A(I,J)=A(I,J)-A(L,J)*YY
  13      CONTINUE
  10      CONTINUE
  40      DO 30 I=1,NA
          IF (B(I).GE.0.0) GO TO 30
          IA=I
          GO TO 50
  30      CONTINUE
          GO TO 31
  50      B(IA)=-B(IA)
          DO 51 J=1,MM
  51      A(IA,J)=-A(IA,J)
          XX=0.00
          JA=0
          DO 52 J=1,MM
          DO 53 I=1,NA
          IF (J.EQ.K(I)) GO TO 52
  53      CONTINUE
          IF (A(IA,J).LE.XX) GO TO 52
          XX=A(IA,J)
          JA=J
  52      CONTINUE
          K(IA)=JA
          B(IA)=B(IA)/XX
          DO 54 J=1,MM
  54      A(IA,J)=A(IA,J)/XX
          DO 55 I=1,NA
          IF (I.EQ.IA) GO TO 55
          YY=A(I,JA)
```

```
        B(I)=B(I)-B(IA)*YY
        DO 56 J=1,MM
56      A(I,J)=A(I,J)-A(IA,J)*YY
55      CONTINUE
        GO TO 40
31      DO 20 I=1,NA
        IA=K(I)
20      BB=BB+F(IA)*B(I)
        DO 21 J=1,MM
        C(J)=0.00
        DO 22 I=1,NA
        IA=K(I)
22      C(J)=C(J)+F(IA)*A(I,J)
21      C(J)=C(J)-F(J)
        WRITE (6,25)
25      FORMAT (1HO, 15X, 22H FOR INITIAL TABLEAU - )
        WRITE (6,26) BB
26      FORMAT (1HO, 16X, 21HOBJECTIVE FUNCTION = , E15.8)
        WRITE (6,27) (K(L), B(L), L=1,NA)
27      FORMAT (1H, 18X, 16HINDEP. VECTOR = , I4, 5X, E15.6)
        CALL SIMPLEX
67      CONTINUE
        STOP
        END
```

```
    $IBFTC  DUAL    NODECK,NOLIST
            SUBROUTINE SIMPEX
**          COMMON A(16,550),B(16),C(550),F(550),K(16),RX(16),
**        1 M,MM,N,NA,BB
      399   QX=C(1)
            JA=1
            DO 300 J=2,MM
            IF (C(J).GE.QX) GO TO 300
            JA=J
            QX=C(J)
      300   CONTINUE
            IF (QX.GE.0.0) GO TO 330
            DO 301 I=1,NA
            IF (A(I,JA).LE.0.0) GO TO 302
            RX(I)=B(I)/A(I,JA)
            GO TO 301
      302   RX(I)=-1.00
      301   CONTINUE
            DO 303 I=1,NA
            IF (RX(I).LT.0.0) GO TO 303
            QA=RX(I)
            II=I
            GO TO 304
      303   CONTINUE
            WRITE (6,307)
      307   FORMAT (1H0, 15X, 20H UNBOUNDED SOLUTION. )
            GO TO 398
      304   IF (II.GE.NA) GO TO 310
            IC=II+1
            DO 305 I=IC,NA
            IF (RX(I).LT.0.0.OR.RX(I).GT.QA) GO TO 305
            IF (RX(I).EQ.QA) GO TO 306
            QA=RX(I)
            II=I
            GO TO 305
      306   IF (K(II).GE.K(I)) GO TO 305
            QA=RX(I)
            II=I
      305   CONTINUE
      310   DX=A(II,JA)
            B(II)=B(II)/DX
            DO 311 J=1,MM
      311   A(II,J)=A(II,J)/DX
            DO 312 I=1,NA
            IF (I.EQ.II) GO TO 312
            DXX=A(I,JA)
            B(I)=B(I)-DXX*B(II)
            DO 313 J=1,MM
            IF (J.EQ.JA) GO TO 314
            A(I,J)=A(I,J)-DXX*A(II,J)
            GO TO 313
      314   A(I,J)=0.00
      313   CONTINUE
      312   CONTINUE
            BB=BB-C(JA)*B(II)
```

```
      DO 315 J=1,MM
      IF (J.EQ.JA) GO TO 315
      C(J)=C(J)-C(JA)*A(II,J)
315   CONTINUE
      C(JA)=0.00
      K(II)=JA
      GO TO 399
330   WRITE (6,331)
331   FORMAT (1HO, 30H THIS IS THE OPTIMUM SOLUTION. )
      WRITE (6,321) BB
321   FORMAT (1H , 20X, 22H OBJECTIVE FUNCTION = , E15.8)
      WRITE (6,322)
322   FORMAT (1HO, 25X, 48HBASIC VARIABLES  AND  VALUES  ARE
     1 AS FOLLOWS )
      WRITE (6,323) (K(I), B(I), I=1,NA)
323   FORMAT (1H , 29X, 14, 12X, E15.8)
398   CONTINUE
      RETURN
      END
```

P-V-T AND ENTHALPY FITTING PROGRAM - PART I

SAMPLE OUTPUT

Index	P (psia)	T (°R)	V (ft^3/mole)

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE

Index	P (psia)	T (°R)	V (ft^3/mole)
1	14.69599984	365.68798720	265.42469632
2	293.91999744	365.68798720	11.59307728
3	440.87998976	365.68798720	7.05650000+
4	587.83999488	365.68798720	4.69597540
5	734.79999488	365.68798720	3.17005208
6	881.75997952	365.68798720	2.00949060-
7	955.23999744	365.68798720	1.60472692
8	1028.71998464	365.68798720	1.34733608+
9	1175.67998976	365.68798720	1.14444251
10	1469.59998976	365.68798720	1.00581990
11	1763.51995904	365.68798720	0.94773212+
12	2057.43996928	365.68798720	0.90649673
13	2351.35997952	365.68798720	0.87646567
14	2645.27992832	365.68798720	0.85330718
15	2939.19997952	365.68798720	0.83388487
16	3673.99993344	365.68798720	0.79763524
17	4408.79996928	365.68798720	0.77108083
18	5878.39995904	365.68798720	0.73296257
19	7347.99986688	365.68798720	0.70686787
20	8817.59993856	365.68798720	0.68577001
21	10287.19992832	365.68798720	0.66860211
22	11756.79991808	365.68798720	0.65509932
23	13226.39966208	365.68798720	0.64292556
24	14695.99973376	365.68798720	0.63243434-
25	14.69599984	401.68798720	291.92793088
26	293.91999744	401.68798720	13.25675200
27	440.87998976	401.68798720	8.34710928
28	587.83999488	401.68798720	5.86273680
29	734.79999488	401.68798720	4.34775612
30	881.75997952	401.68798720	3.31388952
31	1028.71998464	401.68798720	2.58871766
32	1175.67998976	401.68798720	2.06140524
33	2057.43996928	401.68798720	1.10119004-
34	2351.35997952	401.68798720	1.03003101
35	2645.27992832	401.68798720	0.97985900-
36	2939.19997952	401.68798720	0.94366154
37	3673.99993344	401.68798720	0.88001050
38	4408.79996928	401.68798720	0.83877044
39	5878.39995904	401.68798720	0.78354889
40	7347.99986688	401.68798720	0.74740716
41	8817.59993856	401.68798720	0.72062619

Index	P (psia)	T (°R)	V (ft^3/mole)
42	10287.19992832	401.68798720	0.69904076
43	11756.79991808	401.68798720	0.68262781+
44	13226.39966208	401.68798720	0.66791201
45	14695.99973376	401.68798720	0.65502898
46	14.69599984	446.68799488	325.07481600
47	440.87998976	446.68799488	9.77075192
48	587.83999488	446.68799488	7.05045192
49	881.75997952	446.68799488	4.32418172
50	1175.67998976	446.68799488	2.97806144
51	1469.59998976	446.68799488	2.20907598
52	1763.51995904	446.68799488	1.75432940
53	2057.43996928	446.68799488	1.48426528
54	2351.35997952	446.68799488	1.31888140
55	2645.27992832	446.68799488	1.20975196
56	2939.19997952	446.68799488	1.13176186
57	3673.99993344	446.68799488	1.01244239
58	4408.79996928	446.68799488	0.94077669
59	5878.39995904	446.68799488	0.85620947
60	7347.99986688	446.68799488	0.80389302
61	8817.59993856	446.68799488	0.76788105
62	10287.19992832	446.68799488	0.74026483
63	11756.79991808	446.68799488	0.71847803
64	13226.39966208	446.68799488	0.70077653
65	14695.99973376	446.68799488	0.68453772
66	14.69599984	491.68798720	358.18600448
67	440.87998976	491.68798720	11.10734784
68	587.83999488	491.68798720	8.11739024
69	734.79999488	491.68798720	6.32771400
70	881.75997952	491.68798720	5.14056616
71	1175.67998976	491.68798720	3.67095884
72	1469.59998976	491.68798720	2.81283468
73	1763.51995904	491.68798720	2.26970526
74	2057.43996928	491.68798720	1.90785216
75	2351.35997952	491.68798720	1.66220692
76	2645.27992832	491.68798720	1.48885980
77	2939.19997952	491.68798720	1.36665870
78	3673.99993344	491.68798720	1.17255772
79	4408.79996928	491.68798720	1.06094695
80	5878.39995904	491.68798720	0.93737278
81	7347.99986688	491.68798720	0.86580721
82	8817.59993856	491.68798720	0.81839531
83	11756.79991808	491.68798720	0.75639931
84	14695.99973376	491.68798720	0.71637201
85	14.69599984	536.68799488	391.18969344
86	293.91999744	536.68799488	18.89150400
87	587.83999488	536.68799488	9.13146064
88	881.75997952	536.68799488	5.89243936
89	1175.67998976	536.68799488	4.28412168
90	1469.59998976	536.68799488	3.33775568

Index	P (psia)	T (°R)	V (ft^3/mole)
91	1763.51995904	536.68799488	2.72385796+
92	2057.43996928	536.68799488	2.30326792
93	2351.35997952	536.68799488	2.00327128
94	2645.27992832	536.68799488	1.78486420
95	2939.19997952	536.68799488	1.62034626
96	3673.99993344	536.68799488	1.35659228
97	4408.79996928	536.68799488	1.20129120
98	5878.39995904	536.68799488	1.02963979
99	7347.99986688	536.68799488	0.93581803
100	8817.59993856	536.68799488	0.87506099
101	11756.79991808	536.68799488	0.79696574
102	14695.99973376	536.68799488	0.74828191-
103	14.69599984	581.68799232	424.26494976
104	440.87998976	581.68799232	13.62519120
105	587.83999488	581.68799232	10.10427568
106	881.75997952	581.68799232	6.57848424
107	1175.67998976	581.68799232	4.83812480
108	1469.59998976	581.68799232	3.80960920
109	1763.51995904	581.68799232	3.13348352
110	2057.43996928	581.68799232	2.66281720
111	2351.35997952	581.68799232	2.32078662
112	2645.27992832	581.68799232	2.06411540
113	2939.19997952	581.68799232	1.86916558
114	3673.99993344	581.68799232	1.54390180
115	4408.79996928	581.68799232	1.34747550
116	5878.39995904	581.68799232	1.12898534
117	7347.99986688	581.68799232	1.01049919+
118	8817.59993856	581.68799232	0.93443355+
119	11756.79991808	581.68799232	0.84087380
120	14695.99973376	581.68799232	0.78244558
121	14.69599984	671.68799232	490.16482816
122	440.87998976	671.68799232	16.01052304
123	734.79999488	671.68799232	9.50388288
124	881.75997952	671.68799232	7.88229656
125	1175.67998976	671.68799232	5.86381976
126	1469.59998976	671.68799232	4.66240376
127	1763.51995904	671.68799232	3.86951816
128	2057.43996928	671.68799232	3.31007856
129	2645.27992832	671.68799232	2.58564800
130	2939.19997952	671.68799232	2.34158822
131	3673.99993344	671.68799232	1.91452956
132	4408.79996928	671.68799232	1.64570172
133	5878.39995904	671.68799232	1.33670738
134	7347.99986688	671.68799232	1.16592329
135	8817.59993856	671.68799232	1.05827516
136	14695.99973376	671.68799232	0.85085824
137	14.69599984	761.68799232	556.02884608
138	440.87998976	761.68799232	18.34925024
139	734.79999488	761.68799232	10.97301888
140	881.75997952	761.68799232	9.13582560

Index	P (psia)	T (°R)	V (ft^3/mole)
141	1175.67998976	761.68799232	6.82635104
142	1469.59998976	761.68799232	5.45714104
143	1763.51995904	761.68799232	4.54881148
144	2057.43996928	761.68799232	3.90691176
145	2645.27992832	761.68799232	3.06377968
146	2939.19997952	761.68799232	2.77638364
147	4408.79996928	761.68799232	1.93807244
148	5878.39995904	761.68799232	1.54613626
149	7347.99986688	761.68799232	1.32816581
150	8817.59993856	761.68799232	1.18995544
151	11756.79991808	761.68799232	1.02198280
152	14695.99973376	761.68799232	0.92392119
153	14.69599984	851.68798720	621.85705984
154	440.87998976	851.68798720	20.66648912
155	734.79999488	851.68798720	12.39846096
156	881.75997952	851.68798720	10.33026000
157	1175.67998976	851.68798720	7.75485800
158	1469.59998976	851.68798720	6.21642176
159	1763.51995904	851.68798720	5.19736348
160	2057.43996928	851.68798720	4.47304640
161	2645.27992832	851.68798720	3.51544812
162	2939.19997952	851.68798720	3.18037816
163	3673.99993344	851.68798720	2.59401392
164	4408.79996928	851.68798720	2.21265500
165	5878.39995904	851.68798720	1.75368486-
166	7347.99986688	851.68798720	1.49012178
167	8817.59993856	851.68798720	1.32103884
168	11756.79991808	851.68798720	1.11693771
169	14695.99973376	851.68798720	0.99784366-
170	-33.50000000	399.68999424	5.64929032
171	-48.80000000	399.68999424	3.78499320
172	-68.30000000	399.68999424	2.65582174
173	-108.10000000	399.68999424	1.34928770+
174	-125.80000000	399.68999424	1.09298807
175	-27.90000000	429.68999424	6.45917832
176	-39.19999968	429.68999424	4.49586588
177	-51.59999936	429.68999424	3.35531672
178	-81.69999936	429.68999424	1.85024428+
179	-104.89999872	429.68999424	1.35572630
180	-23.90000000	459.68999424	7.19107024
181	-33.00000000	459.68999424	5.10695504
182	-42.50000000	459.68999424	3.89865168
183	-65.60000000	459.68999424	2.33520766
184	-86.69999872	459.68999424	1.65392418
185	-20.90000000	489.68999424	7.88701552
186	-28.50000000	489.68999424	5.70335096
187	-36.19999968	489.68999424	4.39865784
188	-55.19999936	489.68999424	2.72028216
189	-72.80000000	489.68999424	1.94810168

```
169 POINTS LESS THAN LAMBDA
 20 POINTS LESS THAN 0.200000E 01

FOR INITIAL TABLEAU -

OBJECTIVE FUNCTION = -0.12188398E 00
        INDEP. VECTOR =    1        0.999904E 00
        INDEP. VECTOR = 174        0.370885E-03
        INDEP. VECTOR = 366        0.980051E-02
        INDEP. VECTOR = 179        0.646026E-03
        INDEP. VECTOR = 175        0.182368E-01
        INDEP. VECTOR = 213        0.977551E-03
        INDEP. VECTOR = 172        0.487458E-02
        INDEP. VECTOR = 362        0.126763E-02
        INDEP. VECTOR = 188        0.406641E-02
        INDEP. VECTOR = 291        0.158537E-02
        INDEP. VECTOR = 374        0.800862E-02
        INDEP. VECTOR = 378        0.128549E-02
        INDEP. VECTOR = 152        0.278642E-02
        INDEP. VECTOR = 359        0.813789E-02
        INDEP. VECTOR =   42        0.162498E-02
        INDEP. VECTOR = 225        0.261378E-02
```

THIS IS THE OPTIMUM SOLUTION.

```
        OBJECTIVE FUNCTION  =  0.76712749E 00

        BASIC VARIABLES     AND     VALUES   ARE AS FOLLOWS
            3                        0.95600888E 00
          358 (-169)                0.26743441E 02
          291 (-102)                0.17338647E 00
          222 (-33)                 0.37807111E 01
            8                        0.27551992E 01
          213 (-24)                 0.22545391E 00
           43                        0.13031078E 00
           11                        0.52058789E 01
           91                        0.46948989E 00
          354 (-165)                0.30890546E 00
          173                        0.46342028E-03
          178                        0.37755528E-03
          118                        0.60112164E 01
          195 (-6)                  0.18879286E 01
          117                        0.35123013E 02
          224 (-35)                 0.16229045E 02
```

P-V-T AND ENTHALPY FITTING PROGRAM - PART II

```
$IBFTC    CLARE     NODECK
          DOUBLE PRECISION G(16,17),S,D,B,SIG,DIV(16),Y(16),Q,AST
          DIMENSION X(16)
    4     FORMAT(1H ,8HSINGULAR)
    5     FORMAT(1H ,5HERROR)
          N=16
          R=10.73147
          READ(5,550) TC,WT,CONST
  550     FORMAT(1H ,3F15.8)
          READ(5,551) N1,N2
  551     FORMAT(1H , 2I3)
          CON=144.0/(WT*778.173)
          DO 52 I=1,N1
          READ(5,53)P,T,V,SG
   53     FORMAT(1H ,3F15.8,F4.1)
          AT=1.0/(V*V)
          AU=AT/V
          AV=AU/V
          AW=AV/V
          AX=AW/V
          EA=EXP(-5.475*T/TC)
          G(I,1)=0.01
          G(I,2)=AT/P*SG
          G(I,3)=AU/P*SG
          G(I,4)=AV/P*SG
          G(I,5)=AW/P*SG
          G(I,6)=AX/P*SG
          G(I,7)-AT*T/P*SG
          G(I,8)=AU*T/P*SG
          G(I,9)=AV*T/P*SG
          G(I,10)=AW*T/P*SG
          G(I,11)=AX*T/P*SG
          G(I,12)=AT*EA/P*SG
          G(I,13)=AU*EA/P*SG
          G(I,14)=AV*EA/P*SG
          G(I,15)=AW*EA/P*SG
          G(I,16)=AX*EA/P*SG
   52     G(I,17)=(P-R*T/V)/P*SG
          DO 300 I=N2,N
          READ(5,53) H,T,V,SG
          AT=CON/V
          AU=AT/V
          AV=AU/V
          AW=AV/V
          AX=AW/V
          EB=5.475*T/TC
          EC=EXP(-EB)
          ET=(2.0+EB)*EC
```

```
        EU=ET+EC
        EV=EU+EC
        EW=EV+EC
        EX=EW+EC
        G(I,1)=0.0
        G(I,2)=2.0*AT*SG
        G(I,3)=1.5*AU*SG
        G(I,4)=4.0*AV/3.0*SG
        G(I,5)=1.25*AW*SG
        G(I,6)=6.0*AX/5.0*SG
        G(I,7)=T*AT*SG
        G(I,8)=T*AU*SG
        G(I,9)=T*AV*SG
        G(I,10)=T*AW*SG
        G(I,11)=T*AX*SG
        G(I,12)=ET*AT*SG
        G(I,13)=EU*AU/2.0*SG
        G(I,14)=EV*AV/3.0*SG
        G(I,15)=EW*AW/4.0*SG
        G(I,16)=EX*AX/5.0*SG
300     G(I,17)=H*SG-CONST
        NN=N+1
        DO 70 J=1,N
70      DIV(J)=ABS(G(1,J))
        DO 71 J=1,N
        DO 71 I=1,N
71      G(I,J)=G(I,J)/DIV(J)
        K=N
60      MAX=1
        Q=ABS(G(1,K))
        DO 65 I=2,K
        IF(ABS(G(I,K)).LT.Q) GO TO 65
        MAX=I
        Q=ABS(G(MAX,K))
65      CONTINUE
        DO 62 J=1,NN
        AST=G(MAX,J)
        G(MAX,J)=G(K,J)
62      G(K,J)=AST
        K=K-1
        IF(K.GE.2) GO TO 60
9       K=N
11      IF(G(K,K).NE.0.0) GO TO 14
16      M=K-1
22      IF(G(M,K).EQ.0.0) GO TO 20
18      DO 19 J=1,K
        S=G(M,J)
        G(M,J)=G(K,J)
19      G(K,J)=S
        S=G(M,NN)
        G(M,NN)=G(K,NN)
        G(K,NN)=S
```

```
       GO TO 14
20     M=M-1
       IF(M.LT.0) GO TO 99
       IF(M.GT.0) GO TO 22
23     WRITE(6,4)
       GO TO 401
14     D=G(K,K)
       DO 26 J=1,K
26     G(K,J)=G(K,J)/D
       G(K,NN)=G(K,NN)/D
       I=K-1
30     IF(G(I,K).EQ.0.0) GO TO 28
27     B=G(I,K)
       DO 29 J=1,K
29     G(I,J)=G(I,J)=B*G(K,J)
       G(I,NN)=G(I,NN)-B*G(K,NN)
28     I=I-1
       IF(I.LT.0) GO TO 99
       IF(I.GT.0) GO TO 30
32     K=K-1
       IF(K.LT.1) GO TO 99
       IF(K.GT.1) GO TO 11
34     IF(G(1,1).NE.0.0) GO TO 36
35     WRITE(6,4)
       GO TO 401
36     G(1,NN)=G(1,NN)/G(1,1)
       DO 40 I=2,N
       SIG=0.0
       NI=I-1
       DO 38 J=1,NI
38     SIG=SIG+G(I,J)*G(J,NN)
40     G(I,NN)=G(I,NN)-SIG
       DO 400 I=1,N
400    Y(I)=G(I,NN)
       DO 63 I=1,N
63     X(I)=Y(I)/DIV(I)
       WRITE (6,55)
55     FORMAT (1HO, 10X, 16HFINAL SOLUTIONS. )
       WRITE(6,56)(X(I),I=1,N)
56     FORMAT(1H ,E15.8)
C      CHECK OF SOLUTIONS.
       READ(5,57) MM,M1
57     FORMAT(1H ,2I4)
       M11=M1+1
       AM=M1
       A1=MM-M1
       SR=0.0
       WRITE(6,213)
213    FORMAT(1H ,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),
      1 9X,6HP.EXP.,8X,7HP.CALC.,7X,8HABS.DEV.,7X,8HPER.DEV.)
       DO 58 J=1,M1
       READ(5,59) P,T,V
```

```
   59    FORMAT(1H ,3F15.8)
         AT=1.0/(V*V)
         AU=AT/V
         AV=AU/V
         AW=AV/V
         AX=AW/V
         EA=EXP(-5.475*T/TC)
         PK=R*T/V+X(2)*AT+X(3)*AU+X(4)*AV+X(5)*AW+X(6)*AX+X(7)
        1 *AT*T+X(8)*AU*T+X(9)*AV*T+X(10)*AW*T+X(11)*AX*T+X(12)
        2 *AT*EA+X(13)*AU*EA+X(14)*AV*EA+X(15)*AW*EA+X(16)*AX*EA
         DEV=ABS(P-PK)
         PERC=DEV*100.0/P
         WRITE(6,61) V,T,P,PK,DEV,PERC
   61    FORMAT(1H ,F15.4,F15.2,4F15.4)
         SR=SR+DEV
   58    SP=SP+PERC
         SRA=SR/AM
         SPE=SP/AM
         WRITE(6,212) SRA,SPE
  212    FORMAT(1H ,9HAVE.DEV.=,F10.6,13HAVE.PER.DEV.=,F10.6)
         SR=0.0
         SP=0.0
         WRITE(6,214)
  214    FORMAT(1H ,15HV(CU.FT./LB.M.),6X,9HT(DEG.R.),9X,6HH.
        1 EXP.,8X,7HH.CALC.,7X,8HABS.DEV.,7X,8HPER.DEV.)
         DO 301 J=M11,MM
         READ(5,59) H,T,V
         AT=CON/V
         AU=AT/V
         AV=AU/V
         AW=AV/V
         AX=AW/V
         EB=5.475*T/TC
         EC=EXP(-EB)
         ET=(2.0+EB)*EC
         EU=ET+EC
         EV=EU+EC
         EW=EV+EC
         EX=EW+EC
         HK=X(2)*2.0*AT+X(3)*1.5*AU+X(4)*4.0*AV/3.0+X(5)*1.25
        1 *AW+X(6)*6.0*AX/5.0+X(7)*T*AT+X(8)*T*AU+X(9)*T*AV+X(10)
        2 *T*AW+X(11)*T*AX+X(12)*ET*AT+X(13)*EU*AU/2.0+X(14)*EV
        3 *AV/3.0+X(15)*EW*AW/4.0+X(16)*EX*AX/5.0
         DEV=ABS(H-HK)
         PERC=DEV*100.0/ABS(H)
         WRITE(6,61) V,T,H,HK,DEV,PERC
         SR=SR+DEV
  301    SP=SP+PERC
         SRA=SR/A1
         SPE=SP/A1
         WRITE(6,212) SRA,SPE
         GO TO 401
   99    WRITE(6,5)
  401    CONTINUE
         STOP
         END
```

P-V-T AND ENTHALPY FITTING PROGRAM - PART II

SAMPLE OUTPUT

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE.

        FINAL SOLUTIONS.
  0.76716072E 00
 -0.10485025E 05
  0.50240222E 04
 -0.48803061E 04
  0.32307928E 04
 -0.10977803E 04
  0.12119481E 02
 -0.45553829E 01
  0.16332147E 02
 -0.15146344E 02
  0.74635761E 01
 -0.21888554E 06
  0.82097618E 06
 -0.77795798E 06
 -0.89290670E 05
  0.21571796E 06

V(ft³/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
265.4247	365.69	14.6960	14.6905	0.0055	0.0371
11.5931	365.69	293.9200	292.3259	1.5941	0.5424
7.0565	365.69	440.8800	437.4977	3.3823	0.7672+
4.6960	365.69	587.8400	584.4301	3.4099	0.5801
3.1701	365.69	734.8000	735.1740	0.3740	0.0509
2.0095	365.69	881.7600	888.5245	6.7645	0.7672-
1.6047	365.69	955.2400	952.6669	2.5731	0.2694
1.3473	365.69	1028.7200	1020.8281	7.8919	0.7672+
1.1444	365.69	1175.6800	1169.5712	6.1088	0.5196
1.0058	365.69	1469.6000	1478.7901	9.1901	0.6253
0.9477	365.69	1763.5200	1749.9913	13.5286	0.7671+
0.9065	365.69	2057.4400	2043.4027	14.0373	0.6823
0.8765	365.69	2351.3600	2336.8584	14.5016	0.6167
0.8533	365.69	2645.2799	2626.0901	19.1899	0.7254
0.8339	365.69	2939.2000	2922.9564	16.2436	0.5527
0.7976	365.69	3673.9999	3653.4062	20.5938	0.5605
0.7711	365.69	4408.8000	4386.2751	22.5248	0.5109
0.7330	365.69	5878.4000	5868.4759	9.9241	0.1688
0.7069	365.69	7347.9998	7301.8981	46.1017	0.6274
0.6858	365.69	8817.5999	8811.6422	5.9578	0.0676
0.6686	365.69	10287.1999	10343.2196	56.0197	0.5446
0.6551	365.69	11756.7999	11786.4904	29.6906	0.2525
0.6429	365.69	13226.3997	13305.2336	78.8339	0.5960

0

V(ft³/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
0.6324	365.69	14695.9996	14808.7418	112.7422	0.7672-
291.9279	401.69	14.6960	14.6964	0.0004	0.0025
13.2568	401.69	293.9200	293.1151	0.8049	0.2739
8.3471	401.69	440.8800	438.4718	2.4082	0.5462
5.8627	401.69	587.8400	583.8883	3.9517	0.6722
4.3478	401.69	734.8000	730.1023	4.6977	0.6393
3.3139	401.69	881.7600	878.9353	2.8247	0.3204
2.5887	401.69	1028.7200	1025.8795	2.8405	0.2761
2.0614	401.69	1175.6800	1174.4077	1.2723	0.1082
1.1012	401.69	2057.4400	2073.2240	15.7840	0.7672-
1.0300	401.69	2351.3600	2366.5034	15.1434	0.6440
0.9799	401.69	2645.2799	2665.5737	20.2938	0.7672-
0.9437	401.69	2939.2000	2953.4209	14.2209	0.4838
0.8800	401.69	3673.9999	3687.5097	13.5098	0.3677
0.8388	401.69	4408.8000	4403.4374	5.3626	0.1216
0.7835	401.69	5878.4000	5862.1262	16.2738	0.2768
0.7474	401.69	7347.9998	7309.2213	38.7785	0.5277
0.7206	401.69	8817.5999	8766.1270	51.4729	0.5838
0.6990	401.69	10287.1999	10269.4102	17.7897	0.1729
0.6826	401.69	11756.7999	11666.6064	90.1935	0.7672+
0.6679	401.69	13226.3997	13150.9639	75.4358	0.5703
0.6550	401.69	14695.9996	14666.8120	29.1877	0.1986
325.0748	446.69	14.6960	14.6967	0.0007	0.0044
9.7708	446.69	440.880	439.7150	1.1650	0.2642
7.0505	446.69	587.8400	585.2897	2.5503	0.4338
4.3242	446.69	881.7600	876.1652	5.5948	0.6345
2.9781	446.69	1175.6800	1166.9556	8.7244	0.7421
2.2091	446.69	1469.6000	1460.5191	9.0809	0.6179
1.7543	446.69	1763.5200	1757.8892	5.6308	0.3193
1.4843	446.69	2057.4400	2057.1726	0.2674	0.0130
1.3189	446.69	2351.3600	2354.0887	2.7287	0.1160
1.2098	446.69	2645.2799	2650.4379	5.1579	0.1950
1.1318	446.69	2939.2000	2951.1535	11.9535	0.4067
1.0124	446.69	3673.9999	3681.8965	7.8965	0.2149
0.9408	446.69	4408.8000	4415.2249	6.4249	0.1457
0.8562	446.69	5878.4000	5862.3538	16.0462	0.2730
0.8039	446.69	7347.9998	7337.7340	10.2658	0.1397
0.7679	446.69	8817.5999	8794.5684	23.0315	0.2612
0.7403	446.69	10287.1999	10273.0477	14.1522	0.1376
0.7185	446.69	11756.7999	11740.3426	16.4573	0.1400
0.7008	446.69	13226.3997	13183.8579	42.5419	0.3216
0.6845	446.69	14695.9996	14754.2316	58.2319	0.3962
358.1860	491.69	14.6960	14.6954	0.0006	0.0041
11.1073	491.69	440.8800	440.0976	0.7824	0.1775
8.1174	491.69	587.8400	586.3886	1.4514	0.2469
6.3277	491.69	734.8000	732.3523	2.4477	0.3331
5.1406	491.69	881.7600	877.8263	3.9337	0.4461
3.6710	491.69	1175.6800	1168.3064	7.3736	0.6272
2.8128	491.69	1469.6000	1459.2208	10.3792	0.7063

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
2.2697	491.69	1763.5200	1751.2328	12.2872	0.6967
1.9079	491.69	2057.4400	2047.5735	9.8665	0.4796
1.6622	491.69	2351.3600	2345.1412	6.2188	0.2645
1.4889	491.69	2645.2799	2646.3940	1.1140	0.0421
1.3667	491.69	2939.2000	2940.0527	0.8527	0.0290
1.1726	491.69	3673.9999	3681.4495	7.4495	0.2028
1.0609	491.69	4408.8000	4422.5828	13.7828	0.3126
0.9374	491.69	5878.4000	5877.9048	0.4951	0.0084
0.8658	491.69	7347.9998	7358.8032	10.8034	0.1470
0.8184	491.69	8817.5999	8831.6737	14.0737	0.1596
0.7564	491.69	11756.7999	11797.3793	40.5795	0.3452
0.7164	491.69	14695.9996	14751.4786	55.4790	0.3775
391.1897	536.69	14.6960	14.6967	0.0007	0.0046
18.8915	536.69	293.9200	294.0320	0.1120	0.0381
9.1315	536.69	587.8400	586.5437	1.2963	0.2205
5.8924	536.69	881.7600	877.4296	4.3304	0.4911
4.2841	536.69	1175.6800	1168.1666	7.5134	0.6391
3.3378	536.69	1469.6000	1458.4344	11.1656	0.7598
2.7239	536.69	1763.5200	1749.9909	13.5291	0.7672+
2.3033	536.69	2057.4400	2042.9281	14.5119	0.7053
2.0033	536.69	2351.3600	2338.3028	13.0572	0.5553
1.7849	536.69	2645.2799	2633.3880	11.8919	0.4496
1.6203	536.69	2939.2000	2930.4448	8.7552	0.2979
1.3566	536.69	3673.9999	3662.2813	11.7187	0.3190
1.2013	536.69	4408.8000	4395.9807	12.8193	0.2908
1.0296	536.69	5878.4000	5857.9833	20.4167	0.3473
0.9358	536.69	7347.9998	7313.9586	34.0412	0.4633
0.8751	536.69	8817.5999	8772.9465	44.6534	0.5064
0.7970	536.69	11756.7999	11782.0466	25.2467	0.2147
0.7483	536.69	14695.9996	14808.7408	112.7411	0.7672-
424.2649	581.69	14.6960	14.6942	0.0018	0.0122
13.6252	581.69	440.8800	440.6240	0.2560	0.0581
10.1043	581.69	587.8400	586.7092	1.1308	0.1924
6.5786	581.69	881.7600	879.6659	2.0941	0.2375
4.8381	581.69	1175.6800	1170.7000	4.9800	0.4236
3.8096	581.69	1469.6000	1460.4964	9.1036	0.6195
3.1335	581.69	1763.5200	1751.9757	11.5443	0.6546
2.6628	581.69	2057.4400	2044.5743	12.8657	0.6253
2.3208	581.69	2351.3600	2338.8712	12.4888	0.5311
2.0641	581.69	2645.2799	2635.3995	9.8805	0.3735
1.8692	581.69	2939.2000	2929.9942	9.2057	0.3132
1.5439	581.69	3673.9999	3663.7606	10.2394	0.2787
1.3475	581.69	4408.8000	4397.8073	10.9927	0.2493
1.1290	581.69	5878.4000	5849.6770	28.7230	0.4886
1.0105	581.69	7347.9998	7291.6287	56.3711	0.7672+
0.9344	581.69	8817.5999	8749.9542	67.6458	0.7672+
0.8409	581.69	11756.7999	11694.6655	62.1344	0.5285
0.7824	581.69	14695.9996	14751.2942	55.2946	0.3763

V(ft^3/lbm)	T(°R)	P.EXP.	P.CALC.	ABS.DEV.	PER.DEV.
490.1648	671.69	14.6960	14.6959	0.0001	0.0007
16.0105	671.69	440.8800	441.6202	0.7403	0.1679
9.5039	671.69	734.8000	735.4067	0.6067	0.0826
7.8823	671.69	881.7600	882.0753	0.3153	0.0358
5.8638	671.69	1175.6800	1175.0034	0.6766	0.0576
4.6624	671.69	1469.6000	1467.5900	2.0100	0.1368
3.8695	671.69	1763.5200	1760.3747	3.1453	0.1784
3.3101	671.69	2057.4400	2053.9768	3.4631	0.1683
2.5856	671.69	2645.2799	2639.9325	5.3475	0.2022
2.3416	671.69	2939.2000	2931.3838	7.8162	0.2659
1.9145	671.69	3673.9999	3668.1355	5.8645	0.1596
1.6457	671.69	4408.8000	4407.2346	1.5654	0.0355
1.3367	671.69	5878.4000	5869.6043	8.7957	0.1496
1.1659	671.69	7347.9998	7328.3234	19.6764	0.2678
1.0583	671.69	8817.5999	8786.3510	31.2489	0.3544
0.8509	671.69	14695.9996	14789.5172	93.5176	0.6363
556.0288	761.69	14.6960	14.6967	0.0007	0.0046
18.3493	761.69	440.8800	442.0574	1.1774	0.2671
10.9730	761.69	734.8000	736.1498	1.3498	0.1837
9.1358	761.69	881.7600	882.6932	0.9332	0.1058
6.8264	761.69	1175.6800	1178.3572	2.6772	0.2277
5.4571	761.69	1469.6000	1472.2877	2.6877	0.1829
4.5488	761.69	1763.5200	1766.7704	3.2504	0.1843
3.9069	761.69	2057.4400	2060.7122	3.2723	0.1590
3.0638	761.69	2645.2799	2648.9890	3.7090	0.1402
2.7764	761.69	2939.2000	2940.9802	1.7802	0.0606
1.9381	761.69	4408.8000	4415.9431	7.1431	0.1620
1.5461	761.69	5878.4000	5901.3717	22.9717	0.3908
1.3282	761.69	7347.9998	7362.3222	14.3224	0.1949
1.1900	761.69	8817.5999	8810.8502	6.7498	0.0765
1.0220	761.69	11756.7999	11759.3624	2.5625	0.0218
0.9239	761.69	14695.9996	14760.3882	64.3885	0.4381
621.8571	851.69	14.6960	14.6973	0.0013	0.0087
20.6665	851.69	440.8800	442.0497	1.1697	0.2653
12.3985	851.69	734.8000	737.0665	2.2665	0.3084
10.3303	851.69	881.7600	884.9898	3.2298	0.3663
7.7549	851.69	1175.6800	1180.5149	4.8349	0.4112
6.2164	851.69	1469.6000	1475.9148	6.3148	0.4297
5.1974	851.69	1763.5200	1770.7612	7.2412	0.4106
4.4730	851.69	2057.4400	2065.7655	8.3255	0.4047
3.5154	851.69	2645.2799	2656.9557	11.6758	0.4414
3.1804	851.69	2939.2000	2956.9020	17.7020	0.6023
2.5940	851.69	3673.9999	3699.1318	25.1319	0.6840
2.2127	851.69	4408.8000	4442.2686	33.4686	0.7591
1.7537	851.69	5878.4000	5923.4963	45.0964	0.7672-
1.4901	851.69	7347.9998	7401.7185	53.7187	0.7311
1.3210	851.69	8817.5999	8872.6271	55.0272	0.6241
1.1169	851.69	11756.7999	11821.3652	64.5653	0.5492
0.9978	851.69	14695.9996	14808.7414	112.7417	0.7672-

AVE.DEV.= 16.921497AVE.PER.DEV.= 0.369233

V(ft^3/lbm)	T(°R)	H.EXP.	H.CALC.	ABS.DEV.	PER.DEV.
5.6493	399.69	-33.5000	-35.1763	1.6763	5.0040
3.7850	399.69	-48.8000	-49.8439	1.0439	2.1392
2.6558	399.69	-68.3000	-66.6788	1.6212	2.3737
1.3493	399.69	-108.1000	-110.1000	2.0000	1.8501+
1.0930	399.69	-125.8000	-125.6945	0.1055	0.0839
6.4592	429.69	-27.9000	-29.1963	1.2963	4.6461
4.4959	429.69	-39.2000	-40.4390	1.2390	3.1607
3.3553	429.69	-51.6000	-52.0589	0.4589	0.8894
1.8502	429.69	-81.7000	-83.7000	2.0000	2.4480+
1.3557	429.69	-104.9000	-104.2450	0.6550	0.6244
7.1911	459.69	-23.9000	-25.0490	1.1490	4.8077
5.1070	459.69	-33.0000	-34.2858	1.2858	3.8963
3.8987	459.69	-42.5000	-43.5769	1.0769	2.5339
2.3353	459.69	-65.6000	-66.9045	1.3045	1.9885
1.6539	459.69	-86.7000	-86.8768	0.1768	0.2039
7.8870	489.69	-20.9000	-21.9468	1.0468	5.0085
5.7034	489.69	-28.5000	-29.6650	1.1650	4.0879
4.3987	489.69	-36.2000	-37.5284	1.3284	3.6695
2.7203	489.69	-55.2000	-56.7617	1.5617	2.8292
1.9481	489.69	-72.8000	-73.9324	1.1324	1.5555

AVE.DEV. = 1.166175 AVE.PER.DEV. = 2.690023

Example Problem:

Use of the two types of constraint linear program is best illustrated by a simple example. Statements to be changed for a particular problem are indicated in the program listings by **.

Approximating Function:

$$P = a_o + a_1 T + a_2 T^2$$

Derived Property:

$$\frac{dP}{dT} = a_1 + 2a_2 T = DP$$

Data:

$$P_i - T_i \qquad i = 1, 30$$

$$DP_i - T_i \qquad i = 1, 10$$

Fitting Constraints:

Minimize the maximum percentage deviation in pressure subject to the maximum absolute error in DP being less than or equal to some specified value.

Part I Program

    M = 40 (total number of data points)

    M1 = 30 (number of P data points)

    M2 = 10 (number of DP data points)

    N = 3 (number of function coefficients)

    CONST = 0.02 (arbitrary maximum error for DP)

The program statements with ** beside them can be replaced by the following.

```
        COMMON  A(4,80), B(4), C(80), F(80), K(4), RX(4), M,
                MM, N, NA, BB
        READ (5,1)  M, M1, M2, N
1       FORMAT (2X, 4I4)
        READ (5,2) CONST
2       FORMAT (1H ,F15.8)
        NA = N + 1
        M11 = M1 + 1
        MM = M + M
        DO 102 I = 1, M1
        READ (5,101) P,T
        WRITE (6,400) I,P,T
101     FORMAT (1H ,2F15.8)
400     FORMAT (1H ,I3,2F15.8)
        F(I) = 1.0
        A(2,I) = 1.0/P
        A(3,I) = T/P
102     A(4,I) = T**2/P
        DO 401 I = M11,M
        READ (5,101) DP,T
        WRITE (6,400) I,DP,T
        F(I) = DP
        A(2,I) = 0.0
```

```
        A(3,I) = 1.0
401     A(4,I) = 2.0*T
```

Note: The COMMON statement for the subroutine must be made

identical to that of the main program.

Required Output Information:

THIS IS THE OPTIMUM SOLUTION

OBJECTIVE FUNCTION = X.XXXX

BASIC VARIABLES AND VALUES ARE AS FOLLOWS

50	X.XXXX
25	X.XXXX
75	X.XXXX
32	X.XXXX

For basic variable indexes greater than M(40), attach
a minus sign and add M. Also, segregate the controlling
data points into their respective types.

BASIC VARIABLES

$$\left.\begin{array}{l} -10 \\ +25 \end{array}\right\} \text{ P points}$$

$$\left.\begin{array}{l} -35 \\ +32 \end{array}\right\} \text{ DP points}$$

The maximum errors in P and DP occur at the data points
having the basic variable indexes above. The maximum per-
centage error in P is the objective value and the maximum
absolute error in DP is equal to the specified constant (0.02).

Note: If the specified value for CONST is too small no

solution may be possible. In the event of this occurr-

ing, the program will print UNBOUNDED SOLUTION and

cease calculating. This print out may also occur

if a mistake is made in setting up the input section

(**) of the program.

Part II Program

This program is simply Gaussian Elimination solution
of a set of linear equations. A section is also included
for checking the data fitting procedure.

The set of linear equations to be solved for the
example problem are;

$$
\begin{bmatrix}
0.01 & -1.0/P_{10} & -T_{10}/P_{10} & -(T_{10})^2/P_{10} \\
0.01 & +1.0/P_{25} & +T_{25}/P_{25} & +(T_{25})^2/P_{25} \\
0.0 & 0.0 & -1.0 & -2.0T_{35} \\
0.0 & 0.0 & +1.0 & +2.0T_{32}
\end{bmatrix}
\begin{bmatrix}
\lambda \\
a_o \\
a_1 \\
a_2
\end{bmatrix}
=
\begin{bmatrix}
-1.0 \\
+1.0 \\
-DP_{35}-0.02 \\
+DP_{32}-0.02
\end{bmatrix}
$$

The use of the indexes and their signs from the Part
I program becomes obvious from the above example. They are
used to solve for the equation coefficients by the above
method.

The program given can be simply modified to solve the
above set of linear equations and the check of solutions
section can be modified and included if desired.

λ should be equal to the maximum percentage deviation in P given by the Part I program if the equations have been solved accurately.

A P P E N D I X   D
EXAMPLE ENTHALPY DEPARTURE CALCULATIONS

Program I

This program utilizes the given variables V and T to calculate P and $(H-H_o)_T$ values. For the proposed equation of state both pressure and enthalpy departure are explicit functions of V and T, therefore the calculations are simple.

Program II

This program utilizes the most useful method of calculating enthalpy departures. The given variables are P and T and the calculated quantities are volume and enthalpy departure. The proposed equation of state is explicit in pressure and, therefore, must be solved by iteration for volume. The calculated volume is then used to solve explicitly for enthalpy departure.

A search interval method of solving for volume was used rather than Newton-Raphson since $(\partial P/\partial V)_T$ values approach zero in the critical region. The method proved quite efficient but the Newton-Raphson method is undoubtedly better provided no calculations are undertaken in the critical region.

ENTHALPY DEPARTURE CALCULATION PROGRAM

TEMPERATURE AND VOLUME GIVEN

```
$IBFTC    CLARE      NOLIST,NODECK
          READ(5,60) N,L,WT,TC
  60      FORMAT(1H , 2I3,2F15.8)
          AL=L
          R=10.73147
          CON=144.0(WT*778.173)
          DO 80 K=1,N
          READ(5,2) X1,X2,X3,X4,X5,X6,X7,X8,X9,X10,X11,X12,
        1 X13,X14,X15
   2      FORMAT(1H ,3E15.8)
          WRITE(6,52)
  52      FORMAT(1HJ,18HEQUATION CONSTANTS)
          WRITE(6,2) X1,X2,X3,X4,X5,X6,X7,X8,X9,X10,X11,X12,
        1 X13,X14,X15
          WRITE(6,30)
  30      FORMAT(1HJ,4X,9HT(DEG.R.),1X,12HV(CU.FT./M.),6X,
        1 7HP(PSIA),6X,7HP.CALC.,1X,12HABS.ER. IN P,1X,
        2 12HPER.ER. IN P,2X,11HH(BTU./LB.),6X,7HH.CALC.,1X,
        3 12HABS.ER. IN H,1X,12HPER.ER. IN H)
          SA=0.0
          SB=0.0
          SC=0.0
          SD=0.0
          DO 20 I=1,L
          READ(5,1) P,T,EXDH,V
   1      FORMAT(1H ,4F15.8)
          EA=EXP(-5.475*T/TC)
          PC=R*T/V +X1/V **2+X2/V **3+X3/V **4+X4/V **5+X5/V
        1 **6+X6*T/V **2+X7*T/V **3+X8*T/V **4+X9*T/V **5+X10*
        2 T/V **6+X11*EA/V **2+X12*EA/V **3+X13*EA/V **4+X14*
        3 EA/V **5+X15*EA/V **6
          AT=CON/V
          AU=AT/V
          AV=AU/V
          AW=AV/V
          AX=AW/V
          EB=5.475*T/TC
          EC=EXP(-EB)
          ET=(2.0+EB)*EC
          EU=ET+EC
          EV=EU+EC
          EW=EV+EC
          EX=EW+EC
```

```
      DH=X1*2.0*AT+X2*1.5*AU+X3*4.0*AV/3.0+X4*1.25*AW+X5*
    1 6.0*AX/5.0+X6*T*AT+X7*T*AU+X8*T*AV+X9*T*AW+X10*T*
    2 AX+X11*ET*AT+X12*EU*AU/2.0+X13*EV*AV/3.0+X14*EW*
    3 AW/4.0+X15*EX*AX/5.0
      ERH=ABS(EXDH-DH)
      PERH=ERH*100.0/ABS(EXDH)
      ERP=ABS(P-PC)
      PERP=ERP*100.0/P
      SA=SA+ERP
      SB=SB+PERP
      SC=SC+ERH
      SD=SD+PERH
   20 WRITE(6,3) T,V,P,PC,ERP,PERP,EXDH,DH,ERH,PERH
    3 FORMAT(1H ,10F13.4)
      SA=SA/AL
      SB=SB/AL
      SC=SC/AL
      SD=SD/AL
   80 WRITE(6,70) SA,SB,SC,SD
   70 FORMAT(1HJ,16HAVE.ABS.ER.IN P=,F15.6/1X,16HAVE.PER.ER.
    1 IN P=,F15.6/1X,16HAVE.ABS.ER.IN H=,F15.6/1X,16HAVE.
      PER.ER.IN H=,F15.6)
      STOP
      END
```

SAMPLE OUTPUT

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE.

EQUATION CONSTANTS
-0.67068028E 04-0.13433947E 05 0.26809945E 05
-0.19713974E 05 0.48385398E 04 0.64013752E 01
0.23022082E 02-0.30632364E 02 0.18616297E 02
-0.11969532E 01-0.79486745E 06 0.36788516E 07
-0.57315353E 07 0.35269793E 07-0.72916886E 06

T (°R)	V(FT³/M.)	P(PSIA)	P.CALC.	ABS.ER. IN P	PER.ER. IN P	H(BTU/LB)	H.CALC.	ABS.ER. IN H	PER.ER. IN H
399.69	5.6493	600.0	601.8779	1.8779	0.3130	-33.5	-39.2949	5.7949	17.2982
399.69	3.7850	800.0	803.0999	3.0999	0.3875	-48.8	-54.9396	6.1396	12.5811
399.69	2.6558	1000.0	1001.5888	1.5888	0.1589	-68.3	-72.3919	4.0919	5.9911
399.69	1.3493	1500.0	1549.7852	49.7852	3.3190	-108.1	-115.7532	7.6532	7.0797
399.69	1.0930	2000.0	2054.5964	54.5964	2.7298	-125.8	-131.2248	5.4248	4.3122
429.69	6.4592	600.0	603.9460	3.9460	0.6577	-27.9	-29.8479	1.9479	6.9818
429.69	4.4959	800.0	806.8676	6.8676	0.8584	-39.2	-41.3890	2.1890	5.5842
429.69	3.3553	1000.0	1001.0652	1.0652	0.1065	-51.6	-53.2968	1.6968	3.2884
429.69	1.8502	1500.0	1513.7437	13.7437	0.9162	-81.7	-85.3647	3.6647	4.4855
429.69	1.3557	2000.0	2005.9376	5.9376	0.2969	-104.9	-105.8132	0.9132	0.8706
459.69	7.1911	600.0	604.9008	4.9008	0.8168	-23.9	-23.7368	0.1632	0.6828
459.69	5.1070	800.0	809.2404	9.2404	1.1550	-33.0	-32.8233	0.1767	0.5354
459.69	3.8987	1000.0	1006.1265	6.1265	0.6127	-42.5	-42.0894	0.4106	0.9660
459.69	2.3352	1500.0	1490.0248	9.9752	0.6650	-65.6	-65.6422	0.0422	0.0643
459.69	1.6539	2000.0	1989.4938	10.5062	0.5253	-86.7	-85.7664	0.9336	1.0768
489.69	7.8870	600.0	604.5000	4.5000	0.7500	-20.9	-19.5611	1.3389	6.4063
489.69	5.7034	800.0	805.6437	5.6437	0.7055	-28.5	-26.8554	1.6446	5.7705
489.69	4.3987	1000.0	1005.8926	5.8926	0.5893	-36.2	-34.4589	1.7411	4.8097
489.69	2.7203	1500.0	1493.7788	6.2212	0.4147	-55.2	-53.5729	1.6271	2.9477
489.69	1.9481	2000.0	1985.1878	14.8122	0.7406	-72.8	-70.9122	1.8878	2.5932

AVE.ABS.ER.IN P = 11.016357
AVE.PER.ER.IN P = 0.835942
AVE.ABS.ER.IN H = 2.474086
ABE.PER.ER.IN H = 4.716272

EQUATION CONSTANTS

```
-0.10485025E 05   0.50240222E 04  -0.48803061E 04
 0.32307928E 04  -0.10977803E 04   0.12119481E 02
-0.45553829E 01   0.16332147E 02  -0.15146344E 02
 0.74635760E 01  -0.21888554E 06   0.82097617E 06
-0.77795797E 06  -0.89290669E 05   0.21571796E 06
```

T (°R)	V(FT³/M.)	P(PSIA)	P.CALC.	ABS.ER. IN P	PER.ER. IN P	H(BTU/LB)	H.CALC.	ABS.ER. IN H	PER.ER. IN H
399.69	5.6493	600.0	596.2191	3.7809	0.6301	-33.5	-35.1763	1.6763	5.0039
399.69	3.7850	800.0	796.8279	3.1721	0.3965	-48.8	-49.8439	1.0439	2.1392
399.69	2.6558	1000.0	998.4659	1.5341	0.1534	-68.3	-66.6788	1.6212	2.3737
399.69	1.3493	1500.0	1554.2834	54.2834	3.6189	-108.1	-110.1000	2.0000	1.8501
399.69	1.0930	2000.0	2054.5127	54.5127	2.7256	-125.8	-125.6945	0.1055	0.0839
429.69	6.4592	600.0	596.9563	3.0437	0.5073	-27.9	-29.1963	1.2963	4.6461
429.69	4.4959	800.0	798.0878	1.9122	0.2390	-39.2	-40.4390	1.2390	3.1607
429.69	3.3553	1000.0	993.2351	6.7649	0.6765	-51.6	-52.0589	0.4589	0.8894
429.69	1.8502	1500.0	1519.1811	19.1811	1.2787	-81.7	-83.7000	2.0000	2.4480
429.69	1.3557	2000.0	2012.5657	12.5657	0.6283	-104.9	-104.2450	0.6550	0.6244
459.69	7.1911	600.0	598.1562	1.8438	0.3073	-23.9	-25.0490	1.1490	4.8077
459.69	5.1070	800.0	800.2609	0.2609	0.0326	-33.0	-34.2855	1.2855	3.8956
459.69	3.8987	1000.0	996.8160	3.1840	0.3184	-42.5	-43.5769	1.0769	2.5339
459.69	2.3352	1500.0	1489.3383	10.6617	0.7108	-65.6	-66.9045	1.3045	1.9885
459.69	1.6539	2000.0	1998.0656	1.9344	0.0967	-86.7	-86.8768	0.1768	0.2039
489.69	7.8870	600.0	598.6911	1.3089	0.2181	-20.9	-21.9468	1.0468	5.0085
489.69	5.7034	800.0	797.6684	2.3316	0.2914	-28.5	-29.6650	1.1650	4.0879
489.69	4.3987	1000.0	996.9613	3.0387	0.3039	-36.2	-37.5284	1.3284	3.6695
489.69	2.7203	1500.0	1489.5745	10.4255	0.6950	-55.2	-56.7617	1.5617	2.8291
489.69	1.9481	2000.0	1990.4604	9.5396	0.4770	-72.8	-73.9324	1.1324	1.5555

AVE.ABS.ER.IN P = 10.263987
AVE.PER.ER.IN P = 0.715285
AVE.ABS.ER.IN H = 1.166160
AVE.ABS.ER.IN H = 2.689979

ENTHALPY DEPARTURE CALCULATION PROGRAM

PRESSURE AND TEMPERATURE GIVEN

```
$IBFTC   CLARE      NOLIST,NODECK
         READ(5,60) N,L,WT,TC
  60     FORMAT(1H ,2I3,2F15.8)
         AL=L
         R=10.73147
         CON=144.0/(WT*778.173)
         DO 80 K=1,N
         READ(5,2) X1,X2,X3,X4,X5,X6,X7,X8,X9,X10,X11,X12,
     1 X13,X14,X15
   2     FORMAT(1H ,3E15.8)
         WRITE(6,52)
  52     FORMAT(1HJ,18HEQUATION CONSTANTS)
         WRITE(6,2) X1,X2,X3,X4,X5,X6,X7,X8,X9,X10,X11,X12,
     1 X13,X14,X15
         WRITE(6,50)
  50     FORMAT(1HJ,6X,7HP(PSIA),4X,9HT(DEG.R.),1X,12HV(CU.
     1 FT./M.),6X,7HV.CALC.,1X,12HABS.ER. IN V,1X,12HPER.
     2 ER. IN V,2X,11HH(BTU./LB.),6X,7HH.CALC.,1X,12HABS.
     3 ER. IN H,1X,12HPER.ER. IN H)
         SA=0.0
         SB=0.0
         SC=0.0
         SD=0.0
         DO 20 I=1,L
         READ(5,1) P,T,EXDH,VE
   1     FORMAT(1H ,4F15.8)
  10     VO=VE
         DELV=0.1*VO
  11     V1=VO-DELV
         V2=VO+DELV
         EA=EXP(-5.475*T/TC)
         PO=R*T/VO+X1/VO**2+X2/VO**3+X3/VO**4+X4/VO**5+X5/VO
     1 **6+X6*T/VO**2+X7*T/VO**3+X8*T/VO**4+X9*T/VO**5+X10
     2 *T/VO**6+X11*EA/VO**2+X12*EA/VO**3+X13*EA/VO**4+X14
     3 *EA/VO**5+X15*EA/VO**6
         P1=R*T/V1+X1/V1**2+X2/V1**3+X3/V1**4+X4/V1**5+X5/V1
     1 **6+X6*T/V1**2+X7*T/V1**3+X8*T/V1**4+X9*T/V1**5+
     2 X10*T/V1**6+X11*EA/V1**2+X12*EA/V1**3+X13*EA/V1**
     3 4+X14*EA/V1**5+X15*EA/V1**6
         P2=R*T/V2+X1/V2**2+X2/V2**3+X3/V2**4+X4/V2**5+X5/V2
     1 **6+X6*T/V2**2+X7*T/V2**3+X8*T/V2**4+X9*T/V2**5+X10
     2 *T/V2**6+X11*EA/V2**2+X12*EA/V2**3+X13*EA/V2**4+X14
     3 *EA/V2**5+X15*EA/V2**6
         EO=PO-P
         E1=P1-P
         E2=P2-P
```

```
         W=ABS(EO)
         X=ABS(E1)
         Z=ABS(E2)
         RR=EO/W
         S=E1/X
         A=E2/Z
         IF(W-1.0E-02) 22,23,23
22       V=VO
         GO TO 15
23       IF(X-1.0E-02) 24,25,25
24       V=V1
         GO TO 15
25       IF(Z-1.0E-02) 26,27,27
26       V=V2
         GO TO 15
27       IF(RR+S) 28,12,28
12       DELV=0.5*DELV
         VO=VO-DELV
         GO TO 11
28       IF(RR+A) 29,16,29
16       DELV=0.5*DELV
         VO=VO+DELV
         GO TO 11
29       DELV=0.8*VO
         GO TO 11
15       CONTINUE
         AT=CON/V
         AU=AT/V
         AV=AU/V
         AW=AV/V
         AX=AW/V
         EB=5.475*T/TC
         EC=EXP(-EB)
         ET=(2.0+EB)*EC
         EU=ET+EC
         EV=EU+EC
         EW=EV+EC
         EX=EW+EC
         DH=X1*2.0*AT+X2*1.5*AU+X3*4.0*AV/3.0+X4*1.25*AW+X5
1        *6.0*AX/5.0+X6*T*AT+X7*T*AU+X8*T*AV+X9*T*AW+X10*
2        T*AX+X11*ET*AT+X12*EU*AU/2.0+X13*EV*AV/3.0+X14*EW*
3        *AW/4.0+X15*EX*AX/5.0
         ERV=ABS(VE-V)
         PERV=ERV*100.0/VE
         ER=ABS(DH-EXDH)
         PER=ER*100.0/ABS(EXDH)
         SA=SA+ERV
         SB=SB+PERV
         SC=SC+ER
         SD=SD+PER
```

```
20        WRITE(6,3)P,T,VE,V,ERV,PERV,EXDH,DH,ER,PER
 3        FORMAT(1H ,10F13.4)
          SA=SA/AL
          SB=SB/AL
          SC=SC/AL
          SD=SD/AL
80        WRITE(6,70) SA,SB,SC,SD
70        FORMAT(1HJ,16HAVE.ABS.ER.IN V=,F15.6/1X,16HAVE.PER.
     1 ER.IN V=,F15.6/1X,16HAVE.ABS.ER.IN H=,F15.6/1X,
     2 16HAVE.PER.ER.IN H=,F15.6)
          STOP
          END
```

SAMPLE OUTPUT

OBJECT PROGRAM IS BEING ENTERED INTO STORAGE.

EQUATION CONSTANTS
-0.67068028E 04 -0.13433947E 05   0.26809945E 05
-0.19713974E 05   0.48385398E 04   0.64013752E 01
 0.23022082E 02 -0.30632364E 02   0.18616297E 02
-0.11969532E 01 -0.79486745E 06   0.36788516E 07
-0.57315353E 07   0.35269793E 07 -0.72916886E-06

P(PSIA)	T (°R)	V(FT^3/M.)	V.CALC.	ABS.ER. IN V	PER.ER IN V	H(BTU/LB)	H.CALC.	ABS.ER. IN H	PER.ER. IN H
600.0	399.69	5.6493	5.6722	0.0229	0.4053	-33.5	-39.1578	5.6578	16.8890
800.0	399.69	3.7850	3.8069	0.0219	0.5786	-48.8	-54.6841	5.8841	12.0575
1000.0	399.69	2.6558	2.6631	0.0073	0.2734	-68.3	-72.2440	3.9440	5.7745
1500.0	399.69	1.3493	1.3973	0.0480	3.5571	-108.1	-113.2006	5.1006	4.7184
2000.0	399.69	1.0930	1.1097	0.0167	1.5271	-125.8	-130.1451	4.3451	3.4540
600.0	429.69	6.4592	6.5103	0.0511	0.7910	-27.9	-29.6324	1.7324	6.2095
800.0	429.69	4.4959	4.5462	0.0504	1.1206	-39.2	-40.9834	1.7834	4.5496
1000.0	429.69	3.3553	3.3604	0.0051	0.1514	-51.6	-53.2288	1.6288	3.1566
1500.0	429.69	1.8502	1.8730	0.0228	1.2305	-81.7	-84.6027	2.9027	3.5529
2000.0	429.69	1.3557	1.3592	0.0035	0.2594	-104.9	-105.6376	0.7376	0.7031
600.0	459.69	7.1911	7.2585	0.0674	0.9375	-23.9	-23.5255	0.3745	1.5670
800.0	459.69	5.1070	5.1783	0.0713	1.3965	-33.0	-32.4005	0.5995	1.8166
1000.0	459.69	3.8987	3.9290	0.0304	0.7788	-42.5	-41.7944	0.7056	1.6602
1500.0	459.69	2.3352	2.3151	0.0201	0.8618	-65.6	-66.1089	0.5089	0.7758
2000.0	459.69	1.6539	1.6448	0.0091	0.5493	-86.7	-86.1085	0.5915	0.6822
600.0	489.69	7.8870	7.9525	0.0655	0.8301	-20.9	-19.4025	1.4975	7.1651
800.0	489.69	5.7034	5.7496	0.0462	0.8105	-28.5	-26.6460	1.8540	6.5051
1000.0	489.69	4.3987	4.4295	0.0308	0.7007	-36.2	-34.2313	1.9687	5.4385
1500.0	489.69	2.7203	2.7065	0.0137	0.5054	-55.2	-53.8120	1.3880	2.5145
2000.0	489.69	1.9481	1.9323	0.0158	0.8105	-72.8	-71.3708	1.4292	1.9631

AVE.ABS.ER.IN V = 0.030997
AVE.PER.ER.IN V = 0.903774
AVE.ABS.ER.IN H = 2.231690
AVE.PER.ER.IN H = 4.557653

EQUATION CONSTANTS

```
-0.10485025E 05  0.50240222E 04-0.48803061E 04
 0.32307928E 04-0.10977803E 04 0.12119481E 02
-0.45553829E 01 0.16332147E 02-0.15146344E 02
 0.74635760E 01-0.21888554E 06 0.82097617E 06
-0.77795797E 06-0.89290669E 05 0.21571796E 06
```

P(PSIA)	T (°R)	V(FT³/M.)	V.CALC.	ABS.ER. IN V	PER.ER. IN V	H(BTU/LB)	H.CALC.	ABS.ER. IN H	PER.ER. IN H
600.0	399.69	5.6493	5.6029	0.0463	0.8203	-33.5	-35.4357	1.9357	5.7782
800.0	399.69	3.7850	3.7628	0.0222	0.5859	-48.8	-50.0922	1.2922	2.6480
1000.0	399.69	2.6558	2.6490	0.0068	0.2564	-68.3	-66.8150	1.4850	2.1742
1500.0	399.69	1.3493	1.4026	0.0533	3.9477	-108.1	-107.2413	0.8587	0.7944
2000.0	399.69	1.0930	1.1097	0.0168	1.5326	-125.8	-124.6072	1.1928	0.9482
600.0	429.69	6.4592	6.4198	0.0394	0.6104	-27.9	-29.3603	1.4603	5.2342
800.0	429.69	4.4959	4.4819	0.0139	0.3101	-39.2	-40.5497	1.3497	3.4432
1000.0	429.69	3.3553	3.3240	0.0313	0.9326	-51.6	-52.4721	0.8721	1.6902
1500.0	429.69	1.8502	1.8815	0.0313	1.6894	-81.7	-82.6598	0.9598	1.1747
2000.0	429.69	1.3557	1.3633	0.0076	0.5579	-104.9	-103.8642	1.0358	0.9874
600.0	459.69	7.1911	7.1658	0.0253	0.3516	-23.9	-25.1313	1.2313	5.1517
800.0	459.69	5.1070	5.1090	0.0020	0.0391	-33.0	-34.2735	1.2735	3.8590
1000.0	459.69	3.8987	3.8831	0.0155	0.3980	-42.5	-43.7288	1.2288	2.8914
1500.0	459.69	2.3352	2.3143	0.0209	0.8960	-65.6	-67.3841	1.7841	2.7197
2000.0	459.69	1.6539	1.6522	0.0017	0.1013	-86.7	-86.9396	0.2396	0.2764
600.0	489.69	7.8870	7.8678	0.0193	0.2441	-20.9	-21.9973	1.0973	5.2502
800.0	489.69	5.7034	5.6843	0.0191	0.3345	-28.5	-29.7563	1.2563	4.4082
1000.0	489.69	4.3987	4.3829	0.0158	0.3589	-36.2	-37.6489	1.4489	4.0025
1500.0	489.69	2.7203	2.6977	0.0226	0.8301	-55.2	-57.1529	1.9529	3.5379
2000.0	489.69	1.9481	1.9380	0.0101	0.5164	-72.8	-74.2211	1.4211	1.9521

```
AVE.ABS.ER.IN V = 0.021049
AVE.PER.ER.IN V = 0.765658
AVE.ABS.ER.IN H = 1.268802
AVE.PER.ER.IN H = 2.946082
```